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I. *The Kinematics of an Electron with an Axis.*

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Introduction.

IT seems that Abraham † was the first to consider in any detail an electron with an axis. Many have since considered spinning electrons, ring electrons, and the like. Compton ‡ in particular suggested a quantized spin for the electron. It remained for Uhlenbeck and Goudsmit § to show how this idea can be used to explain the anomalous Zeeman effect. The assumptions they had to make seemed to lead to optical and relativity doublet separations twice as large as those observed ||.

The purpose of the following paper, which contains the results mentioned in my recent letter to 'Nature' ¶, is to investigate the kinematics of an electron with an axis on the basis of the restricted theory of relativity. The main fact used is that the combination of two "Lorentz transformations without rotation" in general is not of the same form but is equivalent to a Lorentz transformation with a rotation.

The physical interest of the result obtained is that it shows that Uhlenbeck and Goudsmit's assumptions really lead to

* Communicated by Prof. N. Bohr, Ph.D., LL.D.

† M. Abraham, *Annalen der Physik*, x. p. 105 (1903).

‡ A. K. Compton, Journ. Frankl. Inst. Aug. 1921, p. 145.

§ Uhlenbeck and Goudsmit, *Naturwissenschaften*, Nov. 20, 1925, p. 953; 'Nature,' Feb. 20, 1926, p. 264.

|| See also: Urly and Bichowski, Proc. Nat. Acad. of Sciences, xii. p. 80 (1926).

¶ 'Nature,' April 10, 1926, p. 514.

the correct doublet separation at the same time as the anomalous Zeeman effect when the problem is treated by the new quantum mechanics *. These explanations do not seem to require anything more of the extra terms in the equations of motion of the electron than that its axis should precess about a magnetic field $\mathbf{H}$ with angular velocity $(e/mc)\mathbf{H}$, that in revolution in an orbit there be some secularly conserved angular momentum, and that the contribution of the electron to this angular momentum be $h/4\pi$.

The above assumptions are not, however, sufficient for more than the first order doublet separation. The complete Sommerfeld formula would seem to require a more complete specification of the extra terms in the equations of motion.

Summary.

In the first four sections of this paper the notation used is explained, the relativity kinematics involved is discussed, and a first approximation to the equations of motion of the electron is considered. The change in the direction of its axis is given by

$$\frac{d\mathbf{w}}{ds} = \left[\left\{ \frac{e}{mc}\mathbf{H} - \frac{e}{mc^2}\frac{\beta}{1+\beta}[\mathbf{v}\times\mathbf{E}] \right\} \times \mathbf{w} \right]. \quad (4{\cdot}122)$$

The Abraham spinning electron is discussed briefly. In spite of its inadequacy it is interesting as showing that the assumptions made are not unreasonable.

In the sixth section the secular changes in an electronic orbit are discussed. The equations obtained are

$$\left.\begin{aligned} \frac{d\Omega}{dt} &= \left[\left(\frac{e}{mc}\mathbf{H} + \frac{\sigma}{K}\mathbf{K}\right)\times\Omega\right], \quad . . \quad (6{\cdot}71) \\ \frac{d\mathbf{K}}{dt} &= \left[\left(\frac{e}{2mc}\mathbf{H} + \frac{\sigma}{K}\Omega\right)\times\mathbf{K}\right]. \quad . . \quad (6{\cdot}72) \end{aligned}\right\}$$

In the seventh section a correspondence principle argument is developed giving approximate Zeeman effect and doublet term values and the Heisenberg theory modification of these values is stated †.

Finally, a summary of the reasoning by which the Uhlenbeck-Goudsmit theory connects the Zeeman effect and doublet separation is given ‡.

* W. Heisenberg and P. Jordan, *Zeit. für Phys.*, xxxvii. p. 266 (1926).

† The Heisenberg theory term values, which were very kindly supplied to me by Dr. Heisenberg, are taken from the paper by him and Professor Jordan (*loc. cit.*).

‡ Uhlenbeck and Goudsmit, *loc. cit.*

1. *Notation.*

In the sequel it is convenient to use in some places ordinary vector notation, letters in heavy type denoting vectors, the same letters with suffixes 1, 2, 3 their components, and in other places tensor notation, with the usual summation convention, e. g. $g_{\mu\nu}\,dx^\nu$ short for $\Sigma_\nu g_{\mu\nu}\,dx^\nu$. It will be well, therefore, to connect the two notations here, as well as to state the units that are adopted, especially as these differ from those used by Eddington *.

The position-vector $\mathbf{r}$ of a particle and the time t at which it is at that position are connected with its four coordinates x^1, x^2, x^3, x^4 by

$$\left.\begin{aligned}\mathbf{r} &= (x^1, x^2, x^3),\\ t &= x^4,\end{aligned}\right\} \quad . \quad . \quad , \quad . \quad (1{\cdot}01)$$

$\mathbf{r}$ is in centimetres, t in seconds. s, the "proper time" for the particle, is given by the relation

$$c^2\,ds^2 = c^2\,dt^2 - d\,\mathbf{r}^2 = g_{\mu\nu}\,dx^\mu\,dx^\nu, \quad . \quad . \quad (1{\cdot}02)$$

where the components of $g_{\mu\nu}$, the "fundamental tensor" of relativity theory, have here, as throughout this paper, their values for "Galilean coordinates," $g_{11} = g_{22}, = g_{33} = -1$, $g_{44} = c^2$, the remaining components vanishing, and where c is the velocity of light.

Let

$$\mathbf{v} = \frac{d\mathbf{r}}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1{\cdot}11)$$

$$\beta = \left(1 - \frac{\mathbf{v}^2}{c^2}\right)^{-\frac{1}{2}} = \left(1 + \frac{1}{c^2}\left(\frac{d\mathbf{r}}{ds}\right)^2\right)^{\frac{1}{2}} = \frac{dt}{ds}, \quad . \quad (1{\cdot}12)$$

so that

$$\left.\begin{aligned}\beta\mathbf{v} &= \left(\frac{dx^1}{ds}, \frac{dx^2}{ds}, \frac{dx^3}{ds}\right),\\ \beta &= \frac{dx^4}{ds}.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1{\cdot}13)$$

The electric intensity $\mathbf{E}$ and scalar potential ϕ are in electrostatic units, the magnetic intensity $\mathbf{H}$ and vector

* A. S. Eddington, 'The Mathematical Theory of Relativity,' p. 170.

potential **A** in electromagnetic units, so that

$$(\nabla . \mathbf{A}) + \frac{1}{c}\dot{\phi} = 0, \quad . \quad . \quad . \quad . \quad (1{\cdot}21)$$

$$\left.\begin{aligned} \mathbf{E} &= -\nabla\phi - \frac{1}{c}\dot{\mathbf{A}}, \\ \mathbf{H} &= [\nabla \times \mathbf{A}], \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1{\cdot}22)$$

and in empty space the field equations are

$$\left.\begin{aligned} (\nabla . \mathbf{H}) &= 0, \\ [\nabla \times \mathbf{E}] + \frac{1}{c}\dot{\mathbf{H}} &= 0, \end{aligned}\right\} \quad . \quad . \quad . \quad (1{\cdot}23)$$

$$\left.\begin{aligned} (\nabla . \mathbf{E}) &= 0, \\ [\nabla \times \mathbf{H}] - \frac{1}{c}\dot{\mathbf{E}} &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad (1{\cdot}24)$$

The four-vector k_μ and anti-symmetrical tensor $F_{\mu\nu}$ of the electromagnetic field are given by

$$\left.\begin{aligned} -\mathbf{A} &= (k_1, k_2, k_3), \\ c\phi &= k_4, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1{\cdot}31)$$

$$\left.\begin{aligned} c\mathbf{E} &= (F_{14}, F_{24}, F_{34}), \\ \mathbf{H} &= (F_{23}, F_{31}, F_{12}), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1{\cdot}32)$$

$F_{\mu\nu} = -F_{\nu\mu}$ and $F^{\mu}{}_{\nu} = \dot{g}^{\mu\sigma} F_{\sigma\nu}$, etc. as usual.

Equations (1·21), (1·22), (1·23), (1·24) become (for Galilean coordinates), as usual,

$$\frac{\partial k_\mu}{\partial x_\mu} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1{\cdot}41)$$

$$F_{\mu\nu} = \frac{\partial k_\mu}{\partial x_\nu} - \frac{\partial k_\nu}{\partial x_\mu}, \quad . \quad . \quad . \quad (1{\cdot}42)$$

$$\frac{\partial F_{\mu\nu}}{\partial x_\sigma} + \frac{\partial F_{\nu\sigma}}{\partial x_\mu} + \frac{\partial F_{\sigma\mu}}{\partial x_\nu} = 0, \quad . \quad . \quad . \quad (1{\cdot}43)$$

$$\frac{\partial F^{\mu\nu}}{\partial x_\nu} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1{\cdot}44)$$

If

$$\left.\begin{aligned} -c\mathbf{H} &= (\Phi_{14}, \Phi_{24}, \Phi_{34}), \\ \mathbf{E} &= (\Phi_{23}, \Phi_{31}, \Phi_{12}), \\ \Phi_{\mu\nu} &= -\Phi_{\nu\mu}. \end{aligned}\right\} \quad . \quad . \quad . \quad (1{\cdot}5)$$

$\Phi_{\mu\nu}$ is also a tensor.

The usual equations of motion of a particle of charge ϵ, rest-mass m take the form

$$\frac{d}{dt}(m\beta\mathbf{v}) = \epsilon\left\{\mathbf{E}+\frac{[\mathbf{v}\times\mathbf{H}]}{c}\right\}, \quad . \quad . \quad . \quad (1{\cdot}71)$$

equivalent to

$$\left.\begin{aligned}\frac{d}{ds}\left(m\frac{d\mathbf{r}}{ds}\right) &= \epsilon\left\{\frac{dt}{ds}\mathbf{E}+\frac{1}{c}\left[\frac{d\mathbf{r}}{ds}\times\mathbf{H}\right]\right\},\\ \frac{d}{ds}\left(mc^2\frac{dt}{ds}\right) &= \epsilon\left(\frac{d\mathbf{r}}{ds}.\mathbf{E}\right),\end{aligned}\right\} \quad (1{\cdot}72)$$

or

$$\frac{d}{ds}\left(m\frac{dx^\mu}{ds}\right) = -\frac{\epsilon}{c}F^\mu{}_\nu\frac{dx^\nu}{ds}. \quad . \quad . \quad . \quad . \quad . \quad (1{\cdot}73)$$

2. *Lorentz Transformations.*

The idea of a Lorentz transformation with velocity $\mathbf{v}$ unrestricted in direction is made precise by the following definition. The coordinate system $(\mathbf{r}', t')$ is said to be obtained from the system $(\mathbf{r}, t)$ by a Lorentz transformation with velocity $\mathbf{v}$ without rotation when the equations of transformation take the form

$$\left.\begin{aligned}\mathbf{r}' &= \mathbf{r}+(\beta-1)\frac{(\mathbf{r}\,.\,\mathbf{v})}{\mathbf{v}^2}\mathbf{v}-\beta\mathbf{v}t,\\ t' &= \beta\left\{t-\frac{(\mathbf{r}\,.\,\mathbf{v})}{c^2}\right\},\end{aligned}\right\} \quad . \quad . \quad (2{\cdot}1)$$

where $\beta=(1-\mathbf{v}^2/c^2)^{-\frac{1}{2}}$. Here, of course, $\mathbf{v}$ has nothing to do with the velocity of a particle as defined in (1·11), but is a constant of the transformation.

It is well known that all transformations leaving the form of (1·02) unaltered are combinations of a translation, including change of zero-point of the time, a space rotation, and a transformation of the form (2·1), while conversely any such combination leaves the form of (1·02) unaltered. If the order in which these are taken is fixed, the resolution is unique.

The combination of two successive transformations of the form (2·1) is not in general of the form (2·1) but can be resolved into a transformation of that form together with a rotation. In particular it follows from the theorem of Roderigues and Hamilton, applied to $(\mathbf{r}, ict)$ space or can easily be shown directly, (*cf.* (3·6) below), that the resultant

of such a Lorentz transformation with velocity $-\mathbf{v}$ followed by one with velocity $\mathbf{v}+\delta\mathbf{v}$, where $\delta\mathbf{v}$ is infinitesimal, resolves into a Lorentz transformation with infinitesimal velocity

$$\left.\begin{aligned} &\beta\left\{\delta\mathbf{v}+(\beta-1)\frac{(\mathbf{v}\,.\,\delta\mathbf{v})}{\mathbf{v}^2}\mathbf{v}\right\} \\ &\text{together with an infinitesimal rotation} \\ &(\beta-1)\frac{[\mathbf{v}\times\delta\mathbf{v}]}{\mathbf{v}^2}. \end{aligned}\right\} \quad . \quad . \quad (2{\cdot}2)$$

The transformation of the electromagnetic field corresponding to (2·1) is

$$\left.\begin{aligned} \mathbf{E}' &= \beta\left\{\mathbf{E}+\frac{[\mathbf{v}\times\mathbf{H}]}{c}\right\}+(1-\beta)\frac{(\mathbf{E}\,.\,\mathbf{v})}{\mathbf{v}^2}\mathbf{v}, \\ \mathbf{H}' &= \beta\left\{\mathbf{H}-\frac{[\mathbf{v}\times\mathbf{E}]}{c}\right\}+(1-\beta)\frac{(\mathbf{H}\,.\,\mathbf{v})}{\mathbf{v}^2}\mathbf{v}. \end{aligned}\right\} \quad . \quad (2{\cdot}3)$$

3. *The kinematical description of the motion of an electron.*

Suppose first that the motion of the electron can be described, to a sufficient approximation, by giving the position at any time in $(\mathbf{r}, t)$ of a system of coordinates moving with the electron; that is, by giving coordinate systems (ρ, τ) in which, at different times in $(\mathbf{r}, t)$, the electron is instantaneously at rest at $\rho=0$, $\tau=0$, and which differ successively from one another by the rotation, supposed definite, which the electron undergoes, as well as by that change of origin and time (τ) direction necessary for the electron still to be instantaneously at rest at $\rho=0$, $\tau=0$ in (ρ, τ). This will fix the system (ρ_1, τ_1) for $t=t_1$ in $(\mathbf{r}, t)$ in terms of (ρ_0, τ_0) for $t=t_0$.

At $t=t_0$ let the electron have position $\mathbf{r}_0$ and velocity $\mathbf{v}_0$, with $\beta_0=(1-\mathbf{v}_0^2/c^2)^{-\frac{1}{2}}$, in $(\mathbf{r}, t)$. Then, by (2·1), that definite system of coordinates $(\mathbf{R}_0, T_0)$ in which the electron is instantaneously at rest at the origin and which is obtained from $(\mathbf{r}, t)$ by a translation and a Lorentz transformation without rotation is given by

$$\left.\begin{aligned} \mathbf{R}_0 &= \mathbf{r}-\mathbf{r}_0+(\beta_0-1)\frac{(\mathbf{r}-\mathbf{r}_0\,.\,\mathbf{v}_0)}{\mathbf{v}_0^2}\mathbf{v}_0-\beta_0\mathbf{v}_0(t-t_0), \\ T_0 &= \beta_0\left\{t-t_0-\frac{(\mathbf{r}-\mathbf{r}_0\,.\,\mathbf{v}_0)}{c^2}\right\}. \end{aligned}\right\} \quad (3{\cdot}1)$$

The system (ρ_0, τ_0) is specified by Eulerian angles $(\phi_0, \theta_0, \psi_0)$ giving its angular position in $(\mathbf{R}_0, T_0)$, so that

$$\left.\begin{aligned}
\rho_{01} &= R_{01}(\cos\phi_0\cos\theta_0\cos\psi_0 - \sin\phi_0\sin\psi_0) \\
&\quad + R_{02}(\sin\phi_0\cos\theta_0\cos\psi_0 + \cos\phi_0\sin\psi_0) \\
&\quad - R_{03}\sin\theta_0\cos\psi_0, \\
\rho_{02} &= R_{01}(-\cos\phi_0\cos\theta_0\sin\psi_0 - \sin\phi_0\cos\psi_0) \\
&\quad + R_{02}(-\sin\phi_0\cos\theta_0\sin\psi_0 + \cos\phi_0\cos\psi_0) \\
&\quad + R_{03}\sin\theta_0\sin\psi_0, \\
\rho_{03} &= R_{01}\cos\phi_0\sin\theta_0 \\
&\quad + R_{02}\sin\phi_0\sin\theta_0 \qquad + R_{03}\cos\theta_0,
\end{aligned}\right\}$$

which will be abbreviated as

$$\rho_{0a} = \zeta_{0ab} R_{0b}, \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}21)$$

while $\tau_0 = T_0$.

The system (ρ_1, τ_1) for $t = t_1 = t_0 + dt_0$ in $(\mathbf{r}, t)$ is specified in the same way in terms of $\mathbf{r}_1 = \mathbf{r}_0 + d\mathbf{r}_0$, $\mathbf{v}_1 = \mathbf{v}_0 + d\mathbf{v}_0$, etc. Let

$$\begin{aligned}
d\zeta_0 = (&d\psi_0\sin\theta_0\cos\phi_0 - d\theta_0\sin\phi_0, \\
&d\psi_0\sin\theta_0\sin\phi_0 + d\theta_0\cos\phi_0, \quad d\phi_0 + d\psi_0\cos\theta_0).
\end{aligned} \quad (3{\cdot}22)$$

Since the electron is instantaneously at rest at the origin in both systems, the infinitesimal transformation from (ρ_0, τ_0) to (ρ_1, τ_1) must be of the form

$$\left.\begin{aligned}
\rho_1 - \rho_0 &= \{[\rho_0 \times \mathbf{l}_0] - \tau_0\mathbf{n}_0\}\, ds_0, \\
\tau_1 - \tau_0 &= -\left\{1 + \frac{(\rho_0 \cdot \mathbf{n}_0)}{c^2}\right\} ds_0,
\end{aligned}\right\} \quad . \quad . \quad (3{\cdot}23)$$

where $dt_0 = \beta_0\, ds_0$ and $\mathbf{l}_0$, $\mathbf{n}_0$ are the angular velocity and linear acceleration of the electron measured in (ρ_0, τ_0) at t_0 in $(\mathbf{r}, t)$.

If

$$\left.\begin{aligned}
l_{0a} &= \zeta_{0ab}\, w_{0b}, \\
n_{0a} &= \zeta_{0ab}\, f_{0b},
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (3{\cdot}24)$$

$\mathbf{w}_0$, $\mathbf{f}_0$ are the angular velocity and acceleration measured in $(\mathbf{R}_0, T_0)$.

By eliminating $(\mathbf{r}, t)$ from equations (3·1) and the similar equations for $(\mathbf{R}_1, T_1)$, (*cf.* 2·2)

$$\left.\begin{aligned}\mathbf{R}_1 &= \mathbf{R}_0 + \frac{(\beta_0-1)}{\mathbf{v}_0^2}[\mathbf{R}_0\times[\mathbf{v}_0\times d\mathbf{v}_0]] \\ &\qquad -\beta_0 T_0\left\{d\mathbf{v}_0+(\beta_0-1)\frac{(\mathbf{v}_0\cdot d\mathbf{v}_0)}{\mathbf{v}_0^2}\mathbf{v}_0\right\},\\ T_1 &= T_0-\frac{\beta_0}{c^2}\left\{\left(\mathbf{R}_0\cdot\left\{d\mathbf{v}_0+(\beta_0-1)\frac{(\mathbf{v}_0\cdot d\mathbf{v}_0)}{\mathbf{v}_0^2}\mathbf{v}_0\right\}\right)\right\}-ds_0,\end{aligned}\right\} \quad . \quad . \quad . \quad (3\cdot3)$$

so that, referred to $(\mathbf{R}_0, T_0)$, $(\mathbf{R}_1, T_1)$ has a rotation

$$(\beta_0-1)\,[\mathbf{v}_0\times d\mathbf{v}_0]/\mathbf{v}_0^2$$

as well as a velocity

$$\beta_0\,d\mathbf{v}_0+\beta_0(\beta_0-1)\,(\mathbf{v}_0\cdot d\mathbf{v}_0)\,\mathbf{v}_0/\mathbf{v}_0^2.$$

Comparing (3·23) and (3·3), using (3·21), (3·22), (3·24),

$$\mathbf{f}_0 ds_0 = \beta_0\left\{d\mathbf{v}_0+(\beta_0-1)\frac{(\mathbf{v}_0\cdot d\mathbf{v}_0)}{\mathbf{v}_0^2}\mathbf{v}_0\right\}, \quad . \quad (3\cdot41)$$

$$\mathbf{w}_0 ds_0 = d\zeta_0+(\beta_0-1)\frac{[\mathbf{v}_0\times d\mathbf{v}_0]}{\mathbf{v}_0^2}, \quad . \quad . \quad . \quad (3\cdot42)$$

If $\mathbf{G}_0$ is the rate of change of angular velocity referred to $(\mathbf{R}_0, T_0)$ at $t=t_0$ in $(\mathbf{r}, t)$, by (3·3), since $\mathbf{w}_1$ is measured in $(\mathbf{R}_1, T_1)$,

$$\frac{\mathbf{w}_1-\mathbf{w}_0}{ds_0}\sim \mathbf{G}_0+\frac{(\beta_0-1)}{\mathbf{v}_0^2}\left[\mathbf{w}_0\times\left[\mathbf{v}_0\times\frac{d\mathbf{v}_0}{ds_0}\right]\right],$$

$$i.\,e. \qquad \mathbf{G}_0=\frac{d\mathbf{w}_0}{ds_0}-\frac{(\beta_0-1)}{\mathbf{v}_0^2}\left[\mathbf{w}_0\times\left[\mathbf{v}_0\times\frac{d\mathbf{v}_0}{ds_0}\right]\right]. \quad . \quad (3\cdot5)$$

This means, *inter alia*, that if an electron were to move in a closed path, and its axis of rotation at each moment did not change its direction in the system of coordinates in which the electron was instantaneously at rest, yet after a cycle the direction would be different. In short, $\mathbf{G}$ and $d\mathbf{w}/ds$ are not the same.

For a change of the coordinate system $(\mathbf{r}, t)$, $\mathbf{w}$ so defined does not change in a simple manner. This difficulty can be got rid of in two ways.

1. If

$$\left.\begin{aligned}(w^1, w^2, w^3) &= \mathbf{w} + (\beta - 1)\frac{(\mathbf{w}\,.\,\mathbf{v})}{\mathbf{v}^2}\mathbf{v},\\ w^4 &= \beta\frac{(\mathbf{w}\,.\,\mathbf{v})}{c^2},\end{aligned}\right\} \quad . \quad . \quad (3{\cdot}61)$$

then w^μ is a four-vector transformed like dx^μ and having zero time component and space components equal to $\mathbf{w}$ in any system in which the electron is instantaneously at rest.

It therefore always satisfies the relation

$$g_{\mu\nu} w^\mu \frac{dx^\nu}{ds} = 0. \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}62)$$

2. If

$$\left.\begin{aligned}(w_{23}, w_{31}, w_{12}) &= \beta\mathbf{w} + (1-\beta)\frac{(\mathbf{w}\,.\,\mathbf{v})}{\mathbf{v}^2}\mathbf{v},\\ (w_{14}, w_{24}, w_{34}) &= -\beta[\mathbf{v}\times\mathbf{w}],\end{aligned}\right\} \quad . \quad (3{\cdot}71)$$

and $w_{\mu\nu} = -w_{\nu\mu}$, $w_{\mu\nu}$ is an antisymmetrical tensor transformed like $F_{\mu\nu}$ and having zero components (w_{14}, w_{24}, w_{34}) and components (w_{23}, w_{31}, w_{12}) equal to $\mathbf{w}$ in any system in which the electron is instantaneously at rest.

It therefore always satisfies the relations

$$w^{\mu\nu}\frac{dx^\nu}{ds} = 0, \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}72)$$

which are equivalent to three independent relations.

Whether the electron has a definite rotation or not, if $\mathbf{w}$ is a vector defining in a system of coordinates in which its centre is instantaneously at rest any directed property such as magnetic moment, equations (3·1), (3·3) will apply and (3·5) can be deduced, giving $\mathbf{G}_0$, the rate of change of $\mathbf{w}$ referred to a system of coordinates in which the electron is instantaneously at rest in terms of $d\mathbf{w}/ds$. (3·6) and (3·7) will also still hold good as well as (3·41). (3·42), of course, would then have no meaning.

The only part of the sequel for which it is necessary that $\mathbf{w}$ should be an actual angular velocity is § 5, in which the model of a spinning spherical shell of electricity is considered.

4. *A first approximation to the rate of change of direction of the axis of the electron.*

Suppose that, to a first approximation, in the coordinate system (R, T) in which the electron's centre is instantaneously at rest,

$$\mathbf{f} = -\frac{e}{m}\mathbf{E}', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4{\cdot}01)$$

$$\mathbf{G} = \lambda[\mathbf{H}' \times \mathbf{w}], \quad . \quad . \quad . \quad . \quad . \quad . \quad (4{\cdot}02)$$

where $\mathbf{E}'$, $\mathbf{H}'$ are the field in (R, T), $-e$ is the charge, m the mass of the electron, and λ a constant not yet determined.

Then it follows by (3·5), (3·41), (2·3), expressing $d^2\mathbf{r}/ds^2$, d^2t/ds^2, $d\mathbf{w}/ds$ in terms of $d\mathbf{r}/ds$, dt/ds, $\mathbf{w}$, $\mathbf{E}$, $\mathbf{H}$, that, to a first approximation,

$$\left.\begin{aligned} \frac{d^2\mathbf{r}}{ds^2} &= -\frac{e}{m}\left\{\frac{dt}{ds}\mathbf{E} + \frac{1}{c}\left[\frac{d\mathbf{r}}{ds} \times \mathbf{H}\right]\right\}, \\ \frac{d^2t}{ds^2} &= -\frac{e}{mc^2}\left(\frac{d\mathbf{r}}{ds} . \mathbf{E}\right), \end{aligned}\right\} \quad . \quad . \quad (4{\cdot}11)$$

which are, of course, equivalent to (1·72), remembering that the electronic charge is $-e$, and

$$\frac{d\mathbf{w}}{ds} = \left[\left\{\left\{\frac{e}{mc} + \beta\left(\lambda - \frac{e}{mc}\right)\right\}\mathbf{H} + \frac{(1-\beta)}{\mathbf{v}^2}\left(\lambda - \frac{e}{mc}\right)(\mathbf{H} . \mathbf{v})\mathbf{v} + \left(\frac{e}{mc^2}\frac{\beta^2}{1+\beta} - \frac{\lambda\beta}{c}\right)[\mathbf{v} \times \mathbf{E}]\right\} \times \mathbf{w}\right]. \quad (4{\cdot}121)$$

This last is considerably simpler when $\lambda = \frac{e}{mc}$, when it takes the form

$$\frac{d\mathbf{w}}{ds} = \left[\left\{\frac{e}{mc}\mathbf{H} - \frac{e}{mc^2}\frac{\beta}{1+\beta}[\mathbf{v} \times \mathbf{E}]\right\} \times \mathbf{w}\right]. \quad (4{\cdot}122)$$

In this case, to the same approximation,

$$\frac{dw^\sigma}{ds} = \frac{e}{mc}F^\sigma{}_\nu w^\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4{\cdot}123)$$

and

$$\frac{dw_{\mu\nu}}{ds} = \frac{e}{mc}\{F^\sigma{}_\nu w_{\sigma\mu} - F^\sigma{}_\mu w_{\sigma\nu}\}. \quad . \quad . \quad (4{\cdot}124)$$

The more complicated forms when $\lambda \neq e/mc$ involving $\mathbf{v}$ explicitly on the right-hand side can be found easily if required.

The first approximation equation (4·124) including the coefficient e/mc can also be deduced from the following assumptions.

To a first approximation :—

1. The equations of motion of the centre of the electron are (1·73)
$$\frac{d^2x^\mu}{ds^2} = \frac{e}{mc} F^\mu{}_\nu \frac{dx^\nu}{ds}.$$
2. The antisymmetrical tensor $w_{\mu\nu}$ has its rate of change given by equations that are invariant for Lorentz transformations.
3. $dw_{\mu\nu}/ds$ is a homogeneous linear function of the field $(F_{\mu\nu})$.
4. $dw_{\mu\nu}/ds$ contains no terms higher than quadratic functions of $w_{\mu\nu}$, dx^μ/ds.
5. The relation $w_{\mu\nu}dx^\nu/ds = 0$ is preserved
$$\left(\text{i. e.} \quad w_{\mu\nu}\frac{d^2x^\nu}{ds^2} + \frac{dw_{\mu\nu}}{ds}\frac{dx^\nu}{ds} = 0\right).$$
6. The relation $w_{\mu\nu}w_{\sigma\tau}g^{\mu\sigma}g^{\nu\tau} = \text{const.}$ is preserved
$$\left(\text{i. e.} \quad w_{\sigma\tau}g^{\mu\sigma}g^{\nu\tau}\frac{dw_{\mu\nu}}{ds} = 0\right).$$

For assumptions 2, 3, and 4 only allow an equation of the form
$$\frac{dw_{\mu\nu}}{ds} = K_{\mu\nu} - K_{\nu\mu},$$
where
$$K_{\mu\nu} = AF^\sigma{}_\nu w_{\sigma\mu} + B\Phi^\sigma{}_\nu w_{\sigma\mu} + CF_{\mu\nu} + D\Phi_{\mu\nu} + EF_{\sigma\nu}\frac{dx^\sigma}{ds}\frac{dx^\tau}{ds}g_{\mu\tau} + F\Phi_{\sigma\nu}\frac{dx^\sigma}{ds}\frac{dx^\tau}{ds}g_{\mu\tau},$$
and A, B, C, D, E, F are constants.

Assumptions 5 and 1 then give $A = e/mc$, $B = 0$, $C = 0$, $D = 0$, and assumption 6 gives $E = 0$, $F = 0$.

Similar assumptions for w_μ lead to a similar result.

The next stage would naturally be to seek the second approximation terms in equations (4·11) of motion of the centre of the electron. There does not, however, appear to be any definite way of finding them as they depend on the assumptions made as to the constitution of the electron. As will appear below, to obtain the observed Zeeman effect

and first order doublet separation it seems only to be necessary that they should be such that there is some "angular momentum" which is conserved when the electron revolves in a central field.

Hamilton's principle does not seem to be applicable as the kinematical conditions do not seem to have any meaning for a variation to an adjacent motion not necessarily kinematically possible. Equations in a Lagrange form with extra terms to preserve the kinematical conditions of the usual form can be obtained. The test of their truth must be whether they can give higher order terms in the doublet separation in agreement with experimental results, which, as is well known, are given to a high approximation by Sommerfeld's formula. The equations can also be put in Appell's form *. Perhaps the assumption that the motion of the electron can be described in terms of its position at any time and a single further vector $\mathbf{w}$ is too restrictive.

5. *The Abraham spinning electron.*

It is interesting to see what some particular model of a spinning electron gives for its equations of motion. The simplest is that of Abraham †, a spinning sphere of electricity. As Uhlenbeck and Goudsmit pointed out, he showed that for a uniform spherical shell the coefficient λ in equation (4·02) is e/mc.

Assume :—

1. The electron is a distribution of charge which, in a Galilean system in which its centre is instantaneously at rest is instantaneously spherically symmetrical and rotating like a rigid body with angular velocity $\mathbf{w}$.

2. In such a system the total couple and total force on the electron due to the external field and to its own field, given by retarded potentials, are zero.

These assumptions differ from those of Abraham only in that they imply a Lorentz contraction of the electron, while his supposed it to remain spherical in a system fixed in the "æther."

It follows, agreeing with Abraham, that for $\mathbf{v}=0$, approximately

$$m\mathbf{f} = -e\mathbf{E} + l\nabla(\mathbf{w}\,.\,\mathbf{H}), \qquad \left.\right\} \quad . \quad . \quad (5{\cdot}1)$$

$$I\frac{d\mathbf{w}}{dt} = cl\,[\nabla \times \mathbf{E}] + l\,[\mathbf{w}\times\mathbf{H}], \qquad \left.\right\} \quad . \quad . \quad (5{\cdot}2)$$

* M. P. Appell, *Comptes Rendus*, 1911, p. 1197.
† M. Abraham, *loc. cit.*

where $-e$ is the total charge, $l\mathbf{w}$ the magnetic moment, and

$$m = \frac{2}{3c^2}\iint\frac{d\rho_1\, d\rho_2}{D},$$

$$I = \frac{1}{2c^2}\iint\left\{\frac{2}{3}\frac{(\mathbf{P}_1\,.\,\mathbf{P}_2)}{D} + \frac{1}{3}\frac{[\mathbf{P}_1\times\mathbf{P}_2]^2}{D^3}\right\} d\rho_1\, d\rho_2,$$

$$l = \frac{1}{3c}\int \mathbf{P}^2\, d\rho.$$

The integrations being over the electron, $d\rho_1$, $d\rho_2$ elements of charge at $\mathbf{P}_1$, $\mathbf{P}_2$ from the centre, while $D^2 = (\mathbf{P}_1 - \mathbf{P}_2)^2$.

For a spherical shell radius a,

$$m = \frac{2}{3}\frac{e^2}{ac^2}, \qquad I = \frac{2}{9}\frac{ae^2}{c^2}, \qquad l = \frac{a^2e}{3c}.$$

The terms neglected in (5·1) and (5·2) are terms in $d\mathbf{f}/dt$, $d^2\mathbf{f}/dt^2$ etc., $d^2\mathbf{w}/dt^2$, $d^3\mathbf{w}/dt^3$ etc., and squares, products, and higher powers of $\mathbf{f}$, $\mathbf{w}$ and their derivatives, as well as terms in the second and higher differential coefficients of the external field.

It is to be noted that if the terms $l\nabla(\mathbf{w}\,.\,\mathbf{H})$, $el[\nabla\times\mathbf{E}] = -l\dot{\mathbf{H}}$, depending on the rates of change of the field are left out, the equations (4·01), (4·02) considered above are obtained with $\lambda = e/mc$.

Further, the term $l\nabla(\mathbf{w}\,.\,\mathbf{H})$ is not that which would be expected to be the force on a small magnet in a non-uniform field. The latter is $l(\mathbf{w}\,.\,\nabla)\mathbf{H}$. The difference between these expressions

$$l(\mathbf{w}\,.\,\nabla)\mathbf{H} - l\nabla(\mathbf{w}\,.\,\mathbf{H}) = -l[\mathbf{w}\times[\nabla\times\mathbf{H}]]$$
$$= -(l/c)[\mathbf{w}\times\dot{\mathbf{E}}],$$

while zero if the electric field in the system of coordinates in which the electron is instantaneously at rest is not changing, is not usually zero.

This model has disadvantages that seem to deprive it of any physical meaning.

(1) If $I\mathbf{w} = h/4\pi$ as will be required,

$$|a\mathbf{w}| = (9c^2/4e^2)\,|I\mathbf{w}|$$
$$\approx 200\,c,$$

which seems absurd.

(2) The term in $\mathbf{fw}^2$ was neglected in equation (5·1). This term would represent a magnetic contribution to the mass, and since there would be no corresponding contribution to the angular momentum, the ratio $\lambda = e/mc$ would be disturbed. Further, it has been assumed that while internal forces constrain the electron so that it always has spherical shape instantaneously in a system in which its centre is at rest, these forces do not contribute to the total force and couple in that coordinate system. This will not in general be true for other coordinate systems.

Since Webster has shown that internal forces can be assumed which will cancel the magnetic mass *, the second objection loses some of its force. Moreover, a rapidly spinning electron would not be expected to remain spherical. This model is, however, interesting as showing that there is nothing inherently impossible about the ratio e/mc.

I think we must look towards the general relativity theory for an adequate solution of the problem of the "structure of the electron"; if indeed this phrase has any meaning at all and if it can be possible to do more than to say how an electron behaves in an external field.

6. *The secular change in the direction of the axis of an electron revolving in an orbit.*

It makes no difference which of $\mathbf{w}$, w^*, w_{ax} is used to find the secular change. If the electron revolves under a central electric field Ze/r^2 and a constant external magnetic field $\mathbf{H}$, from (4·122) approximately

$$\frac{d\mathbf{w}}{dt} = \left[\left\{ \frac{e}{mc}\mathbf{H} - \frac{e^2}{mc^2}\frac{1}{2}\left[\mathbf{v}\times\frac{\mathbf{r}Z}{r^3}\right] \right\} \times \mathbf{w} \right]. \quad . \quad (6\cdot1)$$

$\mathbf{K} = m[\mathbf{r}\times\mathbf{v}]$ is the angular momentum of revolution, and can be supposed nearly constant during one revolution, so the secular change in the direction of the spin axis is given by rotation

$$\frac{e}{mc}\mathbf{H} + \frac{1}{2}\frac{e^2}{mc^2}\frac{\overline{Z}}{\overline{r^3}}\mathbf{K}, \quad . \quad . \quad . \quad . \quad . \quad (6\cdot2)$$

where $\overline{Z/r^3}$ is a time mean over a revolution. The occurrence of the factor "1/2" in the second part of (6·1) is due to the difference between $\mathbf{G}$ and $d\mathbf{w}/ds$ caused by the rotation between $(\mathbf{R}_0, T_0)$ and $(\mathbf{R}_1, T_1)$. If the expression for $\mathbf{G}$ were taken instead of (6·1) to be $d\mathbf{w}/ds$, as might be done in the

* D. L. Webster, Phys. Rev. ix. p. 484 (1917).

hope that such "relativity rotation" would prove small, then the secular rotation would seem to be

$$\frac{e}{mc}\mathbf{H}+\frac{e^2}{mc^2}\frac{\overline{Z}}{r^3}\mathbf{K}, \quad . \quad . \quad . \quad . \quad . \quad (6{\cdot}3)$$

or if $\lambda=e/2mc$,

$$\frac{e}{2mc}\mathbf{H}+\frac{e^2}{2mc^2}\frac{\overline{Z}}{r^3}\mathbf{K}. \quad . \quad . \quad . \quad . \quad (6{\cdot}4)$$

It is to be noted that, for a Coulomb field, (Z independent of r),

$$\frac{1}{2}\frac{e^2}{mc^2}\frac{\overline{Z}}{r^3}\mathbf{K}=\sigma$$

is equal to the rate of precession of the perihelion of the orbit in its own plane due to the Sommerfeld relativity effect.

The secular change in the orbit will be the relativity plus screening precession in its own plane, the Larmor precession of its normal about the external magnetic field, and the effect of the unknown second order terms in equations (4·11). If there is to be any "angular momentum" that is conserved at all and the effect is not zero, this effect can hardly be other than some small deformation of the orbit and a rotation of the normal proportional to $\mathbf{w}$. That is, the change in direction of the orbit normal will be a rotation of the form

$$\frac{e}{2mc}\mathbf{H}+\varpi\mathbf{w}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6{\cdot}5)$$

where ϖ depends on the shape and size of the orbit only.

In the absence of external field the equations giving the secular change in plane of the orbit and in $\mathbf{w}$ would then be

$$\left.\begin{aligned}\frac{d\mathbf{w}}{dt}&=\frac{\sigma}{K}[\mathbf{K}\times\mathbf{w}],\\ \frac{d\mathbf{K}}{dt}&=\varpi[\mathbf{w}\times\mathbf{K}],\end{aligned}\right\}$$

so that

$$\frac{d}{dt}\left(\mathbf{K}+\frac{K}{\sigma}\varpi\mathbf{w}\right)=0.$$

$\mathbf{K}+(K/\sigma)\varpi\mathbf{w}$ is what is secularly unchanged. If and only if $(K/\sigma)\varpi$ is the same for all orbits, can this be divided into the angular momentum of the orbit and an angular momentum independent of the orbit to be attributed to the electron.

If $(K/\sigma)\varpi\mathbf{w}=\Omega$, it would be natural to call Ω the angular momentum of the electron. (6·5) becomes

$$\frac{e}{2mc}\mathbf{H}+\frac{\sigma}{K}\Omega, \quad . \quad . \quad . \quad . \quad . \quad (6\cdot6)$$

and the equations to determine secular changes of the orbital plane and electronic axis are

$$\left.\begin{aligned}\frac{d\Omega}{dt}&=\left[\left(\frac{e}{mc}\mathbf{H}+\frac{\sigma}{K}\mathbf{K}\right)\times\Omega\right], \quad . \quad (6\cdot71)\\ \frac{d\mathbf{K}}{dt}&=\left[\left(\frac{e}{2mc}\mathbf{H}+\frac{\sigma}{K}\Omega\right)\times\mathbf{K}\right] \quad . \quad (6\cdot72)\end{aligned}\right\}$$

It is to be noted that using the equation (5·1) obtained from the model of the Abraham electron and averaging just gives (6·72) with $\Omega=I\,\mathbf{w}$.

If $m\mathbf{f}_0=-e\mathbf{E}_0+(Ie/mc)(\mathbf{w}\,.\,\nabla)\mathbf{H}_0$ is used instead of (5·1),

$$\frac{d\mathbf{K}}{dt}=\left[\left(\frac{e}{2mc}\mathbf{H}+\frac{\sigma}{K}2\,I\,\mathbf{w}\right)\times\mathbf{K}\right]$$

would be obtained instead of (6·72). However, as $\mathbf{K}+2\,I\mathbf{w}$ would then, in the absence of external field, be conserved, it would be natural to put $2I\mathbf{w}=\Omega$ and still obtain (6·71), (6·72).

The form of these equations depends only on that of (6·2) and on there being an "angular momentum" secularly conserved in the absence of external magnetic field of which part is the ordinary angular momentum of revolution and part, constant in magnitude, can be assigned to the electron.

7. *The application of the correspondence principle to obtain approximate term values.*

In order to compare with observation, the term values that would be obtained for an electron moving in central electric field Ze/r^2 under a small external magnetic field $\mathbf{H}$ will be obtained.

The first approximation will be the Keplerian ellipse, the term values being

$$-\frac{RZ^2}{n^2},$$

where R is the Rydberg number, n the total quantum number.

Next the orbit precesses in its own plane with the Sommerfeld relativity precession giving the term

$$Z^4 Rx^2\left(\frac{3}{4}\frac{1}{n^4}-\frac{1}{n^3 k}\right),$$

where

$$x = 2\pi e^2/ch = 7{\cdot}29.10^{-3} \quad \text{and} \quad Rx^2Z^4/n^2k^2 = \sigma/2\pi c,$$

while the normal to the orbit and the spin axis precess with angular velocity

$$\frac{\sigma}{K}\mathbf{J}, \quad \text{where } \mathbf{J} = \mathbf{K}+\Omega$$

about the direction **J**, while **J** precesses about **H** with angular velocity

$$\frac{e}{mc}\mathbf{H}\frac{(\Omega\,.\,\mathbf{J})}{J}+\frac{e}{2mc}\mathbf{H}\frac{(\mathbf{K}\,.\,\mathbf{J})}{J},$$

since for small **H**, (6·71), (6·72) give first

$$\left.\begin{aligned}\frac{d\Omega}{dt} &= \frac{\sigma}{K}[\mathbf{J}\times\Omega],\\ \frac{d\mathbf{K}}{dt} &= \frac{\sigma}{K}[\mathbf{J}\times\mathbf{K}],\end{aligned}\right\}$$

and then, averaging over the first rotation,

$$\frac{d\mathbf{J}}{dt} = \frac{e}{mc}[\mathbf{H}\times\mathbf{J}]\frac{(\Omega\,.\,\mathbf{J})}{\mathbf{J}^2}+\frac{e}{2mc}[\mathbf{H}\times\mathbf{K}]\frac{(\mathbf{K}\,.\,\mathbf{J})}{\mathbf{J}^2}.$$

Whether **H** is small or not equations (6·71), (6·72) are just those which would be obtained if the system were Hamiltonian with perturbation function, in addition to the Sommerfeld relativity correction,

$$F = \frac{\sigma}{K}(\mathbf{K}\,.\,\Omega)+\frac{e}{mc}(\mathbf{H}\,.\,\Omega)+\frac{e}{2mc}(\mathbf{H}\,.\,\mathbf{K}).$$

Thus in any case, term values F/ch will give the line frequency differences that correspond to equations (6·71), (6·72), where F is the mean value of F over the motion.

For **H** small, writing $K=kh/2\pi$, $J=jh/2\pi$, $\Omega=rh/2\pi$, $(\mathbf{J}\,.\,\mathbf{H})/H=mh/2\pi$, and expressing the cosines in terms of k, j, r, and m, the term value is

$$\frac{1}{ch}\left\{\frac{j^2-k^2-r^2}{2kr}\frac{rh}{2\pi}\sigma+\left(\frac{eH}{2mc}\right)\frac{mh}{2\pi}\left\{\frac{k^2+j^2-r^2}{2j^2}+2\frac{(r^2+j^2-k^2)}{2j^2}\right\}\right\},$$

i. e.

$$Z^4Rx^2\left\{\frac{j^2-k^2-r^2}{2n^3k^3}\right\}+m\frac{O_{\mathrm{H}}}{c}\left\{\frac{k^2+j^2-r^2}{2j^2}+2\frac{(r^2+j^2-k^2)}{2j^2}\right\}.$$

This gives, collecting all the terms, term value

$$-\frac{RZ^2}{n^2}+Z^4Rx^2\left(\frac{3}{4}\frac{1}{n^4}-\frac{1}{n^3k}\right)+Z^4Rx^2\left(\frac{j^2-k^2-r^2}{2n^3k^3}\right)$$
$$+m\frac{O_{\mathrm{H}}}{c}\left\{\frac{k^2+j^2-r^2}{2j^2}+2\frac{(r^2+j^2-k^2)}{2j^2}\right\}. \quad (7{\cdot}1)$$

For $\Omega=h/4\pi$, $r=\frac{1}{2}$.

Starting from the treatment of the motion of a particle in a Coulomb field due independently to Pauli and Dirac, Heisenberg and Jordan (*loc. cit.*) have shown that on the new theory the above formula must be replaced by

$$-\frac{RZ^2}{n^2}+Z^4Rx^2\left(\frac{3}{4}\frac{1}{n^4}-\frac{1}{n^3(k+\frac{1}{2})}\right)$$
$$+Z^4Rx^2\left(\frac{j(j+1)-k(k+1)-r(r+1)}{2n^3k(k+\frac{1}{2})(k+1)}\right)$$
$$+m\frac{O_{\mathrm{H}}}{c}\left\{\frac{k(k+1)+j(j+1)-r(r+1)}{2j(j+1)}\right.$$
$$\left.+2\frac{(r(r+1)+j(j+1)-k(k+1))}{2j(j+1)}\right\}$$
$$\ldots \quad (7{\cdot}2)$$

where $r=\frac{1}{2}$

$n=1, 2, 3 \ldots$

$k=0, 1, \ldots (n-1)$

$j=k+\frac{1}{2}$ or $k-\frac{1}{2}$ unless $k=0$, when $j=\frac{1}{2}$

$m=-j, -j+1, \ldots, 0, \ldots, j-1, j,$

except that they have not proved that the third term

$$Z^4Rx^2\left(\frac{j(j+1)-k(k+1)-r(r+1)}{2n^3k(k+\frac{1}{2})(k+1)}\right)$$

takes the form it should for S-terms, i.e. $k=0$, $j=\frac{1}{2}=r$, viz.

$$Z^4Rx^2\frac{1}{2n^3(k+\frac{1}{2})}. \quad \ldots \quad (7{\cdot}3)$$

The last term of (7·2) gives the anomalous Zeeman effect correctly.

If the form (7·3) be granted for the S-term, the second and third terms give the "relativity" fine structure correctly according to Uhlenbeck and Goudsmit's scheme with the

observed doublet separation. In fact, if $Z=1$ these two terms reduce to

$$Rx^2\left\{\frac{3}{4}\frac{1}{n^4}-\frac{1}{n^3(k+1)}\right\} \quad \text{for } j=k+\tfrac{1}{2},$$

$$Rx^2\left\{\frac{3}{4}\frac{1}{n^4}-\frac{1}{n^3k}\right\} \quad \text{for } j=k-\tfrac{1}{2},\ k\neq 0.$$

In general the coefficients Z of the different terms in (6·2) will be affected by different screening constants as they arise as averages of different expressions. In any case the doublet separation, the difference of the term values for the same n, k, and different j is

$$Z^4Rx^2/n^3k(k+1).$$

It is to be noted that if instead of the correct expression (6·2), involving the kinematical rotation of the axis discussed above, expression (6·3) had been used, the anomalous Zeeman effect would have been obtained correctly, but twice the observed doublet separation; if expression (6·4), the correct doublet separation but a normal Zeeman effect.

Finally the value $\Omega=h/4\pi$ is necessary for doublets to be obtained (as against triplets, etc., Heisenberg, *loc. cit.*).

8. *A summary of the logical train by which the Goudsmit-Uhlenbeck theory connects the anomalous Zeeman effect with the optical and relativity doublets and accounts for them both as manifestations of the magnetic properties of the electron.*

Starting from the idea that the anomalous Zeeman effect may be explained by the electron itself having a magnetic moment, it is seen that Landé g-values different from unity can be obtained by supposing that the axis of the electron precesses about a magnetic field with angular velocity other than the Larmor rotation. In fact angular velocity e/mc, twice the Larmor precession, must be assumed. If it be assumed that it has such a precession about the magnetic field in a system of axes in which its centre is instantaneously at rest, the secular rate of change of direction of its axis when it revolves in an orbit can be found. Assuming that there is some total angular momentum that is secularly conserved, that which the electron itself adds to that of the orbit having magnitude $h/4\pi$, the secular motion of the system can be found. An approximate formula for the doublet and Zeeman effect separations follows. The new quantum mechanics of Heisenberg transforms this into a formula

which fits the observed doublet separations and Zeeman effect exactly, as far as first order terms in the relativity correction are sufficient.

In conclusion, I wish to express my appreciation of the encouragement and help of Professor Bohr and Dr. Kramers. My thanks are due to Dr. Pauli and Dr. Heisenberg for their helpful criticism.

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Note added later.

Since the above was written Frenkel has published a paper* in which he shows how the consistency of the Zeeman effect and multiplet structure can be obtained from a similar Lagrange function with the same kinematical conditions. (3·72, 1·02.)

Perhaps I may be allowed to state a little more fully than above the position as it appears to me. The difficulty is that if we use Hamilton's principle we must define or take as defined varied motions in which the kinematical conditions are not satisfied, and the equations cannot be interpreted in the above way as representing a rotation in the ordinary sense. Equations for the variations of the "velocities corresponding to quasi-coordinates" $w_{\mu\nu}$ or their equivalent must be assumed in the form

$$\delta dw_{\mu\nu} = d\delta w_{\mu\nu} + g^{\sigma\tau}(\delta w_{\mu\sigma}\, dw_{\tau\nu} - dw_{\mu\sigma}\,\delta w_{\tau\nu}), \qquad (9{\cdot}2)$$

where $dw_{\mu\nu}$ means $w_{\mu\nu}\,ds$, and $\delta w_{\mu\nu}$ are the independent variations, if the analogy with ordinary mechanics is to remain. "True coordinates" giving rise to (9·2) can be found as a kind of formal extension of Eulerian angles (*e. g.* the equations (9·5) below with $d\zeta_{\mu\nu}$ replaced by $w_{\mu\nu}\,ds$ would lead to (9·2)), but there seems to be no physical interpretation of them. I have tried to use as Lagrange function, originally obtained in connexion with the Abraham electron model,

$$\mathrm{L} = -\tfrac{1}{2}mg_{\mu\nu}\frac{dx^\mu}{ds}\frac{dx_\nu}{ds} + \frac{e}{c}k_\mu\frac{dx^\mu}{ds} + \tfrac{1}{4}Iw_{\mu\nu}w_{\sigma\tau}g^{\mu\sigma}g^{\nu\tau} - \frac{\lambda}{2}w_{\mu\nu}F^{\mu\nu}. \qquad (9{\cdot}3)$$

If $\lambda = \dfrac{Ie}{mc}$ the kinematical conditions are automatically satisfied to the first order—as the argument given above

* J. Frenkel, *Zeit. für Physik*, xxxvii. p. 243.

shows. As we have already contemplated motions not satisfying the kinematical conditions, it is natural to see what happens if they are discarded altogether. The equations then take the wonted Hamiltonian form, and the usual methods of solution can be applied safely at any rate to the first order.

Frenkel uses a Lagrange function equivalent to

$$L = \frac{e}{c} k_\mu \frac{dx^\mu}{ds} + \tfrac{1}{4} I w_{\mu\nu} w_{\sigma\tau} g^{\mu\sigma} g^{\nu\tau} + \frac{\lambda}{2} w_{\mu\nu} F^{\mu\nu}.$$

The change of sign in the last term may be brought about by denoting by $w_{\mu\nu}$ what I have called $w_{\nu\mu}$, or by $-e$ what I have called e. Use of the kinematical conditions, which is now necessary if nonsense is to be avoided, leads him to first order secular equations identical with those obtained in § 6 of this paper.

The following results more general than those in § 3 which I obtained at the same time may be of interest.

We can suppose the electron's configuration to be determined by giving the position of its centre, $x^\mu{}_0$, and the orientation of a Galilean coordinate system ξ^μ with origin at its centre, which can be described as in (3·1), (3·21) in terms of $\theta, \phi, \psi, \mathbf{v}$; $\beta = (1 - \mathbf{v}^2/c^2)^{-\frac{1}{2}}$, where $\mathbf{v}$ is not now necessarily the velocity of the centre. Thus

$$\xi^\mu = A^\mu{}_\nu (x^\nu - x^\nu{}_0),$$

where $A^\mu{}_\nu$ depend on $\theta, \phi, \psi, \mathbf{v}$. After interval ds,

$$\xi^{\mu\prime} = A^\mu{}_\nu{}' (x^\nu - x^\nu{}_0{}') = A^\mu{}_\nu{}' y^\mu.$$

Defining $y^{\mu\prime}$ by

$$\xi^{\mu\prime} = A^\mu{}_\nu y^{\nu\prime},$$

it follows that

$$y^{\mu\prime} = d\zeta^\mu{}_\nu y^\nu + y^\mu,$$

where $d\zeta_\nu^\mu$ may, without prejudice, be called the "rotation" of the electron. It is easily shown that

$$\delta d\zeta^\mu{}_\nu = d\delta\zeta^\mu{}_\nu + \delta\zeta^\mu{}_\sigma d\zeta^\sigma{}_\nu - d\zeta^\mu{}_\sigma \delta\zeta^\sigma{}_\nu \quad . \quad . \quad (9{\cdot}4)$$

if $\theta, \phi, \psi, \mathbf{v}$ be regarded as (six) "true coordinates" capable of variation independently of $x^\mu{}_0$, while

$$(d\zeta_{23}, d\zeta_{31}, d\zeta_{22}) = \beta\, d\boldsymbol{\zeta} + \frac{(1-\beta)}{\mathbf{v}^2} \mathbf{v}(d\boldsymbol{\zeta} \,.\, \mathbf{v}) + \frac{(1-\beta)}{\mathbf{v}^2} [\mathbf{v} \times d\mathbf{v}],$$

$$(d\zeta_{14}, d\zeta_{24}, d\zeta_{34}) = -\beta d\mathbf{v} - \beta [\mathbf{v} \times d\boldsymbol{\zeta}] + \frac{\beta(1-\beta)}{\mathbf{v}^2} \mathbf{v}(\mathbf{v} \,.\, d\mathbf{v}),$$

$$. \quad . \quad . \quad (9{\cdot}5)$$

where $d\boldsymbol{\zeta}$ is given by (3·22).

The condition that if initially

$$(\beta \mathbf{v},\ \beta) = \frac{dx^\nu}{ds}$$

this shall continue to hold is

$$\frac{dx^\nu}{ds}\frac{d\zeta_\nu^\mu}{ds} = -\frac{d^2x^\nu}{ds^2}, \quad . \quad . \quad . \quad . \quad . \quad (9{\cdot}6)$$

which are four independent conditions replacing (3·72), (1·02).

If these hold the equations reduce to those of § 3, with

$$\frac{d\zeta^{\mu\nu}}{ds} = w^{\mu\nu} + \frac{1}{c^2}\left\{\frac{dx^\nu}{ds}\frac{d^2x^\mu}{ds^2} - \frac{dx^\mu}{ds}\frac{d^2x^\nu}{ds^2}\right\}. \quad . \quad (9{\cdot}7)$$

If this picture is adopted, $d\zeta_{\mu\nu}$, with (9·6) as kinematical conditions, would seem to replace $w_{\mu\nu}ds$ as the fundamental rotation tensor, as the former retains some physical meaning when (9·6) does not hold (in which case $w_{\mu\nu}$ might perhaps be *defined* by (9·7)) and on this picture $d\zeta_{\mu\nu}$ satisfies (9·4), while $w_{\mu\nu}$ does not in general satisfy (9·2). Equations (9·6) do not seem to be suitable to be kinematical conditions connected with a Lagrange function.

Taking a Lagrange function of the form (9·3), $d\zeta_{\mu\nu}/ds$ replacing $w_{\mu\nu}$,

$$\mathrm{L} = -\tfrac{1}{2}mg_{\mu\nu}\frac{dx^\mu}{ds}\frac{dx^\nu}{ds} + \frac{e}{c}k_\mu\frac{dx^\mu}{ds} + \tfrac{1}{4}I\frac{d\zeta_{\mu\tau}}{ds}\frac{d\zeta_{\sigma\nu}}{ds}g^{\mu\sigma}g^{\nu\tau} - \tfrac{1}{2}\frac{Ie}{mc}\frac{d\zeta_{\mu\nu}}{ds}F^{\mu\nu}, \quad (9{\cdot}8)$$

equations (9·6) are approximately satisfied better than (3·72) (1·02) with (9·3). To the first order this Lagrange function and the corresponding Hamiltonian function seem to be sufficient.

II. *On the Use of Donnan's Membrane Equilibrium Theory for the Determination of the Charge of Colloid Particles.* *By* Niels Bjerrum *.

IN a paper in the January number of this Journal (Phil. Mag. i. Jan. 1926) Herman Rinde has criticised my paper: "Zur Theorie der osmotischen Drucke, der Membranpotentiale und der Ausflockung von Kolloiden" (*Zeitschr. physik. Chem.* cx. p. 656, 1924).

* Communicated by the Author.

He goes so far as to write : " Unfortunately there are in this paper a number of errors, and I will here call attention to only a few of them."

However, apart from the pointing out of two errata, all Rinde's specified objections seem to me to be unjustified and of no value. Concerning the " errors " which Rinde claims to have found, but which he has not specified, I feel myself entitled to suppose that they are of the same nature as the " errors " which he mentions.

Rinde's first objection relates to the method used by me to calculate the intrinsic charge of the colloid particles in chromium hydroxide sols. He quotes the following sentence as being incomprehensible : " Fügt man zu p, die Zahl der adsorbierten Anionen, q, die Zahl der freien Ladungen, so erhält man die Gesamtladung der Kolloidpartikeln pro Chromatom." As far as I can see, the difficulty found by Rinde in understanding this sentence must be due to the fact that he has not made himself familiar with my terminology, which rather differs from the one used by him. Rinde works with colloid sulphur particles. He takes for granted that these colloid particles are in themselves uncharged and acquire a negative electric charge only through adsorption of anions. In my paper, on the contrary, the colloid particles in chromium hydroxide are considered as large ions with big positive intrinsic charges (as polyvalent complex positive ions). The big positive charges of these colloid-ions attract by electric forces some of the small negative ions present in the solution (Cl^-, NO_3^-) and bind (" adsorb ") them. Consequently the adsorption of ions does not produce the charges of the particles, but on the contrary it diminishes the free charges of the particles by partially neutralizing their original intrinsic charges. To calculate the intrinsic charge of my particles (" Die Gesamtladung der Kolloidpartikeln ") one has to add to the free positive charge (q) the charge (p), neutralized through adsorption of negative ions. This is the simple meaning of the above quoted sentence, which Rinde has not been able to understand.

I willingly admit that the use of the term " Gesamtladung der Kolloidpartikeln " for what in this paper is called " intrinsic charge of the particles " may be a little misleading ; but every careful reader of my paper will be able to understand what is meant by this expression. The above quoted sentence, which Rinde finds unintelligible, may, for instance, be considered as representing its definition.

Concerning the colloid sulphur particles with which Rinde works, I am inclined to think that they also possess a definite intrinsic charge of their own. It seems to me improbable that their strongly-bound charges should be due to adsorbed anions such as $S_2O_3^{--}$, SO_3^{--}, SO_4^{--}, etc. In my opinion a colloid sulphur particle is to be considered as a large anion consisting of a firm construction of sulphur atoms and owing its charge to the presence of radicals such as $-S^-$ or $-SO_3^-$, etc. These radicals are firmly chemically bound, nearly in the same way as, for instance, the carboxylic radicals $-CO^-$ in organic anions. In a solution of sodium chloride such a negative sulphur particle will, of course, attract and bind sodium cations ("adsorb them"). This adsorption will diminish the effective free charge of the particle, but the intrinsic charge will remain unchanged and only be partially neutralized or screened.

The second error, which Rinde claims to have found in my paper, consists in my assumption that the free charge q of the colloid particles is a constant. From my experimental material he concludes that q is not constant. All the conclusions which I have drawn from this assumption—for instance, that the number of chromium atoms per chromium hydroxide particle is 1000, etc.—are therefore according to him wrong. If Rinde had, however, read my paper more carefully, he would have perceived that I do not generally suppose q to be a constant. On page 673, for instance, I write that it is to be expected that q diminishes with increasing electrolyte concentration, owing to increased adsorption of anions.

According to the above developed conceptions of the origin of the charge of the colloid particles, it is not q, the free charge of the particles, but $(p+q)$, the intrinsic charge, which I expect to be a constant. And even this constancy is not unconditionally claimed in my paper. On page 677 I write that the values of $p+q$ are not as constant as might perhaps have been expected; but as the values of $p+q$ show a rather regular decrease with decreasing acidity, I try to explain this lack of constancy by hydrolysis.

In order to get a general view, I have admittedly on page 670 considered q as a constant and from this assumption developed laws for the osmotic pressure. In view of what I write later on in my paper, it is strange that Rinde has not understood that I have used this assumption only as a useful approximation.

Concerning Rinde's criticism of my calculation of n, the

number of chromium atoms in the particles, it is rather curious that he has not noticed that it is unnecessary to claim absolute constancy of q in order to arrive at my result. From table 6, page 672, it is to be concluded that n must lie between 500 and 2000, if q is not to change more than in the ratio 1 : 4 nor increase with increasing electrolyte concentration.

Rinde has calculated the values of q in three of my experiments, using as a basis for the calculation my membrane potential measurements. He finds values nearly twice as large as the values which I have calculated, using as a basis measurements of osmotic pressure. Concerning this disagreement, he writes: "I think that this depends, among other things, upon the fact that Bjerrum has used the osmotic pressure for the calculation of q, which is not permissible for these large particles according to Hammarsten's and this research."

As I cannot guess the meaning of the words "among other things" in the quoted sentence, it is not possible for me to refute the attack latent in these words. But I wish to point out that in a separate chapter of my paper (p. 673) I have especially emphasized the lacking agreement between membrane potentials and osmotic pressures, which causes Rinde's q-values calculated from potentials to deviate from my q-values calculated from pressures. I try to explain this disagreement by the inaccuracy of the assumptions used for the activity and the osmotic effect of small ions in presence of highly charged colloid particles. Later on (pp. 682–3) I return to the same point. Rinde seems to ignore these remarks of mine.

In my paper I wrote that I preferred to calculate q from pressures and not from potentials, because all my other calculations were based on the osmotic pressure. I wish to point out here that I used the pressures not only for this reason but also because the data for the osmotic pressures were more ample and more accurate than the data for the potentials, and last, but not least, because I considered that the interionic forces might make the calculation from the potentials less safe than the calculation from the pressures. The measurements quoted on page 667 in my paper seem to indicate that a certain caution is necessary in using membrane potentials for these calculations.

In the above quoted sentence, Rinde writes that my method of calculation is not permissible according to Hammarsten's and his research. I must confess that it has not been possible for me to arrive at the same conclusion from the experimental data in Hammarsten's and Rinde's papers.

Admittedly Hammarsten's experimental results are most interesting, but I cannot see that it is as yet satisfactorily shown how they are to be explained, and the experimental support found in Rinde's own paper is only poor. From the osmotic pressure measurements he calculates that the sol (0·10–0·20) contains the smallest particles, and the sol (0·40–) the largest. Contrary to this, an examination under the ultramicroscope shows him that the sol (0·10–0·20) contains very large particles and the sol (0·40) only amicrons. From this disagreement Rinde concludes that it is not permissible to use osmotic pressures for the determination of the size of his particles nor for the determination of q. However, the difference in size calculated from the osmotic pressures is only small (the ratio is roughly as 7·4 to 8·6), and it is to be remembered that even an amount of large particles easily observable in the ultramicroscope may be of little influence on the mean size of the particles. Only a more quantitative ultramicroscopic research would be convincing.

In my opinion, the question concerning the choice of membrane potentials or osmotic pressures for calculation of q is not as yet settled. It cannot be said with certainty what is right and what is wrong.

The only parts of my paper which Rinde has criticised with a certain justification are the formulæ (22) and (23). He points out that these formulæ have a false form, and speaks in this connexion of correcting "a mathematical error." However, if he had taken the trouble to investigate the question a little closer, he could easily have convinced himself that the faults are only errata, as all the calculations in the following Table are made with the right formulæ. A few months after the publication of my paper I have myself corrected these two errata (*Zeitschr. physik. Chem.* cxiii. p. 336, 1924).

Equally unnecessary seems to me Rinde's final remark that my formula (23) "....is of very little importance, partly because, as already stated, the osmotic pressure cannot be used for such calculation and partly because the cases where the series development can be broken off at the first term, as Bjerrum has done, should be considered as exceptions." In my paper I not only give the material for a complete series development (p. 669, formula 12), but I also point out under what conditions it is allowable to break off at the first term, and concerning the formula (17) I state explicitly that it has been necessary only in two of my experiments to take the second term into consideration.

Copenhagen,
8th April, 1926.

III. *On the* 1*s*–*md Series of Cæsium and the other Alkali Metals.* *By* G. M. Shrum, *M.A., Ph.D.*, N. M. Carter, *M.Sc., and* H. W. Fowler, *B.A., Department of Physics, University of British Columbia* *.

[Plate I.]

Introduction.

ACCORDING to the Bohr Rubinowicz selection principle, the combination series 1*s*–*md* is forbidden, since it is the result of an interorbital transmission requiring a change of two units in the azimuthal quantum number. It is now generally established that this selection principle holds rigidly only when there are no disturbing influences, such as an external electric field, due either to adjacent charged ions, or an ordinary applied difference of potential. Bohr † has shown that such an external force introduces new constituent harmonic vibrations, in addition to the vibration already present in the simple central orbit, thereby violating the restriction $\Delta k = \pm 1$. Owing to these considerations, the splitting-up of a line into Stark effect components, or the appearance of entirely new or forbidden spectral lines in the presence of an external field, has usually been regarded as a confirmation of the selection principle.

Recent experiments, however, seem to indicate that the presence of an external field cannot explain all the violations of the selection principle. Experiments by Foote and others ‡ have proved beyond doubt that these transfers can take place in the absence of an applied external field. They observed the radiation of the combination lines 1*s*–2*d*, 2*d*′ of potassium in the space shielded from the electrostatic field. Absorption experiments by Datta § on potassium, and Sowerby and Barratt ‖ on the alkali metals, have shown that the combination lines 1*s*–*md* are very easily absorbed. In these absorption experiments there can be no possibility of an external field, or effects due to neighbouring ions, while the effect of neighbouring atoms was diminished by working at very low pressures. Van Vleck ¶ has pointed out that in some cases the appearance of the forbidden lines

* Communicated by the Authors.
† Bohr, Phil. Mag. xliii. p. 1114 (1922).
‡ Foote, Meggers, and Mohler, Astrophys. Journ. lv. p. 145 (1922).
§ Datta, Proc. Roy. Soc. ci. A, p. 544 (1922).
‖ Sowerby and Barratt, Proc. Roy. Soc. cx. A, p. 192 (1926).
¶ Van Vleck, Bull. Nat. Res. Council, 54, p. 132.

may be explained by the introduction of coupling forces between negative electrons; and therefore the process is probably intimately connected with the emission of lines due to the simultaneous jumping of two electrons.

In view of the importance of these latter considerations, it seemed desirable to extend the experimental data as far as possible. The present investigation comprises a study of the excitation, in the carbon arc, of the series $1s$–md for the alkali metals, especially that due to cæsium, since previous attempts have failed to bring out these lines for Cs, although it has been shown that the alkali metals are all able to absorb the combination lines $1s$—md.

Experimental Method and Apparatus.

The excitation was produced by means of an ordinary hand-feed carbon arc, operated from a 135-volt D.C. main, having suitable rheostats in series with the arc, so that the current in the circuit was approximately 1·8 amperes, and the potential drop across the electrodes registered from 20 to 30 volts. Hilger "High Purity" carbon electrodes 7 mm. diam. were used, and the lower carbon was made the positive pole. The length of the arc was 8 mm., and light from the central axial portion only was focussed on the slits. The cæsium salt was obtained from Dr. E. H. Archibald, of the Department of Chemistry. It was found that the carbonate fused into the hot carbons more readily than the chloride, and therefore gave much better results.

A Hilger constant deviation glass spectrograph was used for the visible region, while a small quartz spectrograph served for the ultra-violet. In front of the slit of each spectrograph an ordinary camera shutter was placed, so arranged that they were operated by a single bulb. It was found that the $1s$–md lines only appeared when the electrodes were well coated with the cæsium salt. As a control instrument, a constant deviation glass spectroscope was set for the line 6848 Å., and all three instruments were illuminated simultaneously from one arc. Intermittent exposures were made by operating the shutter-bulb. The shutters were opened only when the line 6848 Å. showed very clearly in the spectroscope. The total exposure ranged from two to six minutes.

The wave-lengths were in all cases measured from two or more plates, using Cs and Fe lines as standards in the visible, and the Cu arc for the ultra-violet.

Experimental Results.

Pl. I. A is an enlarged reproduction of one of the spectrograms showing the lines in the visible region. The line 6894·7 Å. does not show clearly in the reproduction, because it was not very dense owing to the falling-off in the sensitivity of the panchromatic plates in this region. Pl. I. B is an enlargement of one of the plates taken with the small quartz spectrograph. In this spectral region four members of the $1s-md$ series appeared on the plates. The dispersion was not sufficient to show the doublet structure of the lines, especially since the longer wave-length component is much weaker and the long exposures required caused a considerable blackening of the plates.

Table I. gives the values of the wave-lengths obtained, and also the values caculated from Fowler's Report on Series Spectra.

TABLE I.

Series notation.	λ observed I.Å.	I.	λ calculated I.Å.
1s–3d.....	6894·7 Å.	0	6894·84 Å.
	6848·6	2	6848·60
1s–4d.....	4425·7	2	4425·70
	4417·4	4	4417·32
1s–5d.....	3836	1	3838·0
			3834·9
1s–6d.....	3594	1	3594·6
			3593·1
1s–7d.....	3467	1	3467·8
			3466·8
1s–8d.....	3391	0	3392·5
			3392·0

From the first two pairs, it will be observed that there is very good agreement between the observed and experimental values. These observed wave-lengths are practically the same as those obtained by Sowerby and Barratt* in their absorption experiments. It would appear that the great difference which they noted between observed and calculated values was due to the fact that they apparently neglected to make the ordinary vacuum correction for their calculated wave-lengths. When this correction is applied, it will be observed that there is an excellent agreement between the

* Sowerby and Barratt, *loc. cit.*

observed and calculated values, and therefore no necessity for a revision of the term values of Cs as they had suggested.

The question of a new line is always associated with that of the purity of the source, and consequently great care was taken to eliminate the possibility of these lines being due to impurities. The spectra were all remarkably pure, although faint lines were observed due to Na, K, Rb, Li, and Ca as impurities. The presence of the Rb line 3591·6 Å. may possibly affect the reading recorded for the Cs line at 3594 Å. The line 4425·7 Å. agrees very well with the line 4425·43 Å. of Ca, but since the strong doublet of the same series at 4425 Å. did not appear on the plates, it was decided that the possibility of this line belonging to Ca was very remote.

A condensed spark was passed between the same electrodes, but none of the lines in question appeared. They do not therefore belong to the spark spectrum of Cs, nor is this type of discharge favourable for their excitation.

Sodium, Potassium, and Rubidium.

The same method of excitation was applied to Na, K, and Rb, and it was found that the corresponding series lines came out. No wave-length determinations for these lines are given, since they were in good agreement with the values already published.

Flame Spectra.

In view of the fact that these 1*s*–*md* lines of Cs came out very readily in the carbon arc when it was well saturated with Cs vapour, it was thought that perhaps similar results might be obtained with an ordinary flame. Flames well saturated with the Cs salt, however, did not give these lines, although the ordinary Cs lines were very intense.

Conclusions.

The exact process of the emission of these lines has not been definitely determined, but a careful study of the conditions most favourable for their excitation seemed to indicate that it was independent of the applied potential and the current strength, and that they could only be excited when the arc was well saturated with Cs vapour. The usual procedure was to strike the arc until the tips of the electrodes became red hot, and then fuse the carbonate into both electrodes. When the arc was subsequently struck, the lines

were always very strong for a few seconds ; then they disappeared, although the ordinary Cs lines remained very strong. There is a possibility that the decomposition of the salt may provide ions that set up the disturbing field, or that these ions may be more easily excited to the *d* levels.

Summary.

1. A very simple and direct method of exciting the 1*s*–*md* combination lines in the alkali metals has been described.

2. By this means six members of the series 1*s*–*md* of cæsium, not previously observed in emission, have been photographed.

3. Wave-length determinations have shown that the observed values are in good agreement with the values calculated from Fowler's Report on Series Spectra.

June 14th, 1926.

IV. *On the Combustion of Carbon Monoxide.*

By C. F. R. Harrison, *B.Sc.*, *and* J. P. Baxter, *B.Sc.**

Introduction.

THE research described in this paper is a continuation of the work on gaseous combustion commenced in 1921 for the purpose of investigating various problems in connexion with the gas-engine.

The primary object was the determination of the velocity of the propagation of flames through explosive mixtures of various gases at constant volume, and the variation of this velocity with change in initial pressure, mixture strength, amount and composition of diluent, etc. It was intended to obtain records of the actual movement of the flame-front in passing from point to point through the gas.

At the outset it was proposed to confine the research to the investigation of the combustion of carbon monoxide, and a plant was erected at the University of Birmingham for the production of this gas in a pure condition, and on a fairly large scale.

The apparatus first employed was designed by Messrs. J. L. Pearson and R. C. A. Anderson, and the credit for the development of the ingenious "Ionized Gap" method of recording flame-speeds is entirely due to Captain Pearson.

* Communicated by Prof. F. W. Burstall, M.Sc., M.A., M.Inst C.E., M.I.Mech.E.

The research was continued by Messrs. A. H. Newey and J. H. Crowe, and an account of the method employed and the results obtained is published in the Philosophical Magazine, June 1925, page 1125.

The research with which this paper deals was commenced in 1924. The authors, after a few months' work with the "Ionized Gap" method, decided to abandon it because they considered that the results obtained were unreliable, and because they desired to investigate the chemical reactions taking place during combustion. It was decided to employ the method suggested originally at the commencement of the research in 1921. This involves the use of platinum resistance thermometers and an Einthoven Galvanometer, and is later described in greater detail.

The bomb in which the gases are exploded is that designed at the commencement of the research by Pearson and Anderson. It consists of two flanged hemispheres bolted together by eighteen $1\frac{1}{4}$ inches nickel-steel bolts, the flanges being $1\frac{1}{2}$ inches thick. The thickness of the walls is $1\frac{1}{4}$ inches and the internal diameter is 16 inches, giving a total capacity of 2015 cubic inches, or about 35 litres. There is a boss at the top of each hemisphere containing gas passages and valve seatings, whilst that on the upper hemisphere carries a large eye-bolt, the lower being screwed on to the single leg which supports the bomb.

Each of the four valves (V, fig. 1) controls two gas passages, those in the upper hemisphere leading to

(1) supplies of compressed air and oxygen;
(2) the mercury manometer and exhaust pump;

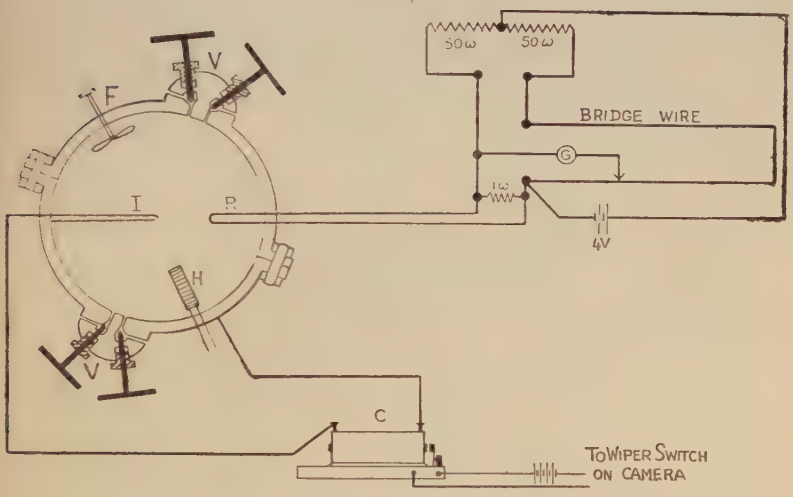
whilst those in the lower lead to

(3) Bourdon Pressure-gauge, and supply of combustible gas;
(4) exit for burnt gases, and supply of pure dry air.

There are, in all, 24 plug-holes, each tapped for $1\frac{1}{4}$-inch gas thread. Each is faced and grooved so that a soft copper washer will make an explosion-tight joint when the plug is screwed home. These holes are distributed around different circles at varying radial angles with the underside of the flange of the hemispheres. At present only four of these are used, viz. for the fan F, ignition plug I, heater plug H, and recording plug R, respectively. The ignition plug is placed directly opposite to the recording plug, and the line joining them makes an angle of approximately 45° with the vertical. The remaining holes are filled with dummies.

The sphere is silvered on the inside, though not polished. During a large number of experiments lasting over several years there has been very little corrosion of this surface, and no carbon has been deposited.

Fig. 1.



The Ignition.

Ignition is effected by means of a spark from an induction-coil C. As the plate falls in the camera it causes a wiper-switch on the oil-plunger to make contact in the primary circuit of the induction-coil, the timing being suitably arranged so that that portion of the record which is required may be obtained on the plate.

The Fan. (Fig. 1, F.)

The fan used for mixing the gases in the sphere, previous to an explosion, consists of a long spindle carrying two collapsible blades at one end and a pulley at the other. While the fan is running it works in a stuffing box filled with lead packing, but during an explosion the spindle is withdrawn against a coned seating making an absolutely gas-tight joint. The fan is driven by a small electric motor.

Mixtures are stirred for twenty minutes, and then allowed to stand for five minutes for turbulence effects to settle. It has been determined that these precautions ensure perfect homogeneity in the mixtures.

The Heater Plug. (Fig. 1, H.)

It was found that after explosions involving the formation of water, the interior of the sphere could not properly be dried by exhausting it several times, refilling it with dry air between the successive exhaustings. The present authors have installed a device consisting of a coil of nickel-chrome wire wound in a cylindrical fire-resisting porcelain former about 3 inches in length and 1 inch diameter. This consumes 2 amps. at 220 volts, and radiates sufficient heat to remove all moisture from the walls of the sphere in about 10 minutes. Used in conjunction with a blast of dry air, complete drying of the interior of the sphere can be effected in a comparatively short time.

The Recording Plug. (Fig. 1, R.)

This plug was designed to fulfil the following requirements :—

(1) It must carry four insulated rods to the interior of the sphere.
(2) It must be perfectly gas-tight and able to withstand the explosion pressure.
(3) The insulation must not be affected by the explosions.

The insulating material used originally was ebonite, but it was found that the pressure and changes in temperature to which it was subjected caused sufficient shrinkage of the material to produce a leak. It was therefore replaced by bakelite, which has so far proved quite satisfactory in every respect.

The plug, which was made in the University workshops, is of mild steel; it is threaded to fit one of the ordinary plug-holes in the sphere. The electrodes are equally spaced about the centre of the plug.

The Method of Filling the Sphere.

(1) *Air.*

When pure dry air is required at pressures up to one atmosphere, it is obtained by drawing fresh air from outside the building through two sulphuric acid bottles followed by a cylindrical drying tube containing fused calcium chloride.

For pressures greater than one atmosphere the air is stored in cylinders over calcium chloride at 100 atmospheres pressure.

(2) *Explosive Gases.*

Up to the present only carbon monoxide, methane, and hydrogen have been used as the explosive gases in these

experiments. The hydrogen and methane were obtained outside the University in cylinders containing 100 cubic feet. The CO is made in the department.

Before entering the sphere each gas is dried by passing it upwards through a vertical cast-iron tube packed with anhydrous calcium chloride, which is constantly renewed. A separate tube is used for each gas; since the rate of flow of gas is kept constant, the explosive mixture is always approximately in the same hygroscopic condition at the commencement of any experiment. Oxygen is dried in a similar manner.

The Exhaust Pump.

This is a Fleuss "Geryk" Vacuum Pump, and is capable of reducing the pressure in the sphere to about 1 cm. of mercury. After each explosion the sphere is exhausted at least twice, and is refilled after each exhaustion with pure dry air to atmospheric pressure. This ensures almost complete removal of the burnt gases—about 1 part in 5000 remains, the error thus involved being negligible.

When it is desired to analyse the exhaust gases for oxides of nitrogen, the total contents of the sphere can be drawn through absorption-tubes if required, the volume of gas being measured by the change in pressure.

The Mercury Manometer.

To measure pressures below 3 atmospheres a mercury manometer is used. This is a glass capillary U tube, the open leg of which is about 10 feet long. The scale is of boxwood and has an error of 1 mm. in 100 cm. It has been found that the composition of a mixture as calculated from the manometer readings agrees closely with that determined by analysis in the Haldane Apparatus. The difference is within the limit of experimental error.

The Bourdon Gauge.

To measure higher pressures a Bourdon Gauge calibrated at the National Physical Laboratory and reading up to 300 lb. per square inch is used. It was re-calibrated, immediately before use in the present researches, on the Standard Mercury Column erected in the department for calibration purposes.

The Recording Circuit.

A schematic diagram of the recording circuit is given in fig. 1. The deflexions of the galvanometer G are proportional to the current passing through it. At the beginning

of an experiment the sliding contact of the bridge is adjusted to the balance position, where there is no galvanometer deflexion. As the resistance of the recording plug alters, owing to the changes in temperature when the flame passes the wire, a small current flows through the galvanometer. This current is proportional to the change in resistance of the recording wire, and therefore approximately proportional to the temperatures of the latter. Corrections for variations in the temperature coefficient of resistance of platinum at different temperatures have to be made in any attempt to calculate actual temperatures.

The Einthoven String Galvanometer has been used throughout the research. When it is desired to determine flame velocity in a mixture, several recording wires are used in parallel, in the same plug, at varying distances from the centre of the sphere. The developed plate shows a series of kicks, indicating the times at which the flame has passed over the various recording wires. Since a time record is obtained on the same plate, flame velocities over the intervals between the wires can be calculated. The results of a series of these determinations are given in Table V. (p. 50).

It has been found most convenient to employ three recording wires: one near the centre, one near the walls, and the third about half-way between.

The results show that there is a considerable decrease in the mean velocity over the second portion in CO mixtures Also the mean flame velocity is much lower in the dry mixtures, bearing out the work of previous investigations. The effect of moisture is so great that, unless the hygroscopic state of the gas is accurately described, results are quite valueless.

The effect of replacing the N_2, in the mixture $2CO + O_2 + 4N_2$, by O_2 is greatly to increase the flame-speed. If CO be used as the diluent the effect is still greater. The effect is due, in all probability, to two causes: (1) the decrease in dissociation which is proportional to the concentration of O_2 and to the square of the concentration of CO; (2) the energy absorbing effect of nitrogen described by Bone and others in a series of papers published in the Proc. Roy. Soc. 1911–1925.

Attempts to measure the flame-speed in Hydrogen-Air mixtures have so far failed, owing to the rapidity of the motion and the violent pressure-waves set up. The results obtained indicate that the flame travels at a speed of 10–20 times greater than it does in a dry CO air-mixture, *i. e.* at a speed of roughly 1000 cm. per second.

The Temperature Records.

Figs. 2–4 show the effect of steadily increasing the concentration of CO in explosive mixtures of CO and air,

Fig. 2.

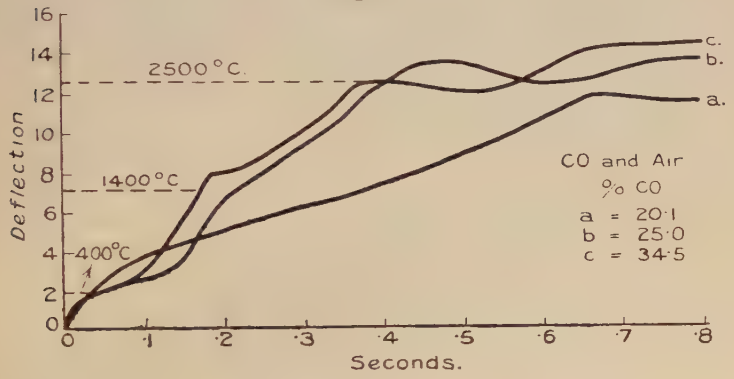


Fig. 3.

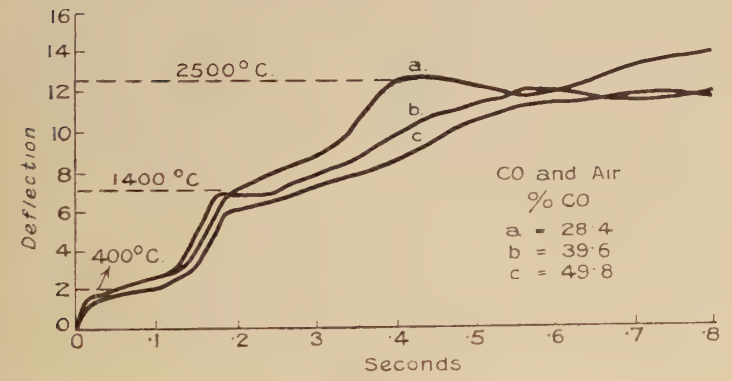
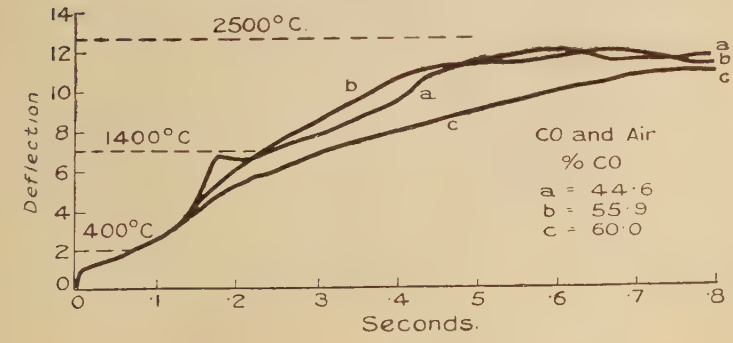


Fig. 4.



keeping the concentration of air constant. The curves, in general, possess one common peculiarity, viz. there is a fairly rapid initial rise of about 400° C. (In the figures given, galvanometer deflexions are plotted vertically against a time basis in seconds. The galvanometer deflexions are approximately proportional to temperatures, a deflexion of 1 unit representing roughly 200° C. The maximum deflexion obtained on the plate is about 7–8 cm.)

As the concentration of CO is increased, the curve takes on the following characteristics :—

(1) The initial rise of 400° C. approximately, already referred to.

(2) A second rapid rise from about 500° C. to about 1400° C. This is not quite so rapid as the first rise.

(3) A third, slower, rise up to the maximum temperature, which lies in the neighbourhood of 2500° C.

(4) This maximum is followed by a fall and a subsequent increase in temperature. It is thought that this increase may be due to the adiabatic compression produced by the combustion of gas in outer layers and by the conduction of heat back along the supports. The latter effect is probably very slight, if it exists at all. It may also be due to the liberation of energy absorbed by nitrogen ; but this seems unlikely, since the same effect is found in mixtures where no nitrogen is present, nor is there any excess of CO to absorb radiant energy.

Dissociation is at a minimum in the case of the 45-per-cent. curve ; and this shows these characteristics most distinctly. In fact, there is a sharply-defined peak at the end of the second rise. As the amount of diluent CO is increased, these characteristics steadily lose their definition, and we find that the curve for the 60-per-cent. mixture agrees quite closely with that of the 20-per-cent.

Fig. 5 shows the effect of varying the mixture strength in CO-oxygen mixtures. The effect is similar to that in the case of CO-air mixtures.

Figs. 6 and 7 illustrate the behaviour of nitrogen as a diluent. The N_2 in the mixture $2CO+O_2+4N_2$ is replaced first by CO and then by O_2. The effect of CO is much greater than that of oxygen, but in both cases there is a more rapid attainment of maximum temperature. This appears to support the theory that nitrogen absorbs energy of radiation, and thus interferes with the ease of combustion.

Fig. 5.

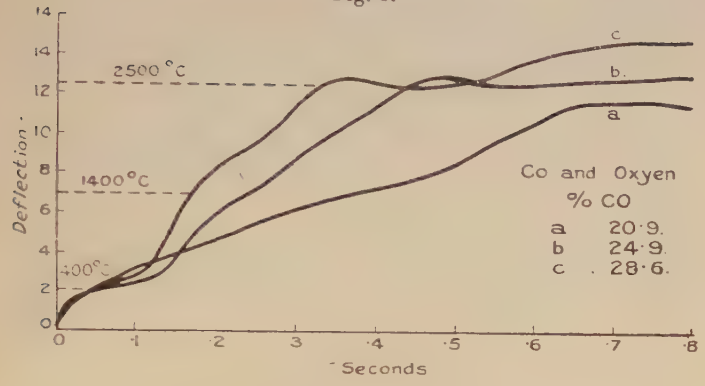


Fig. 6.

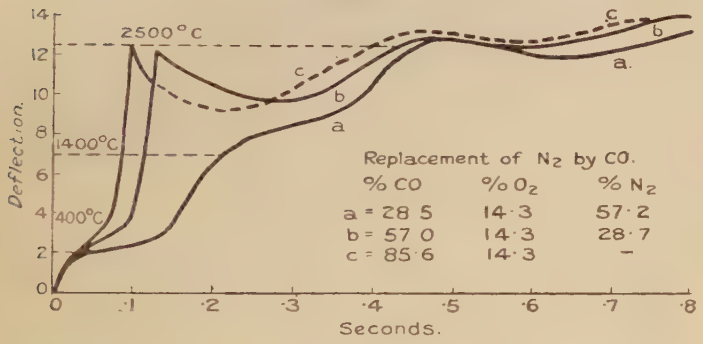
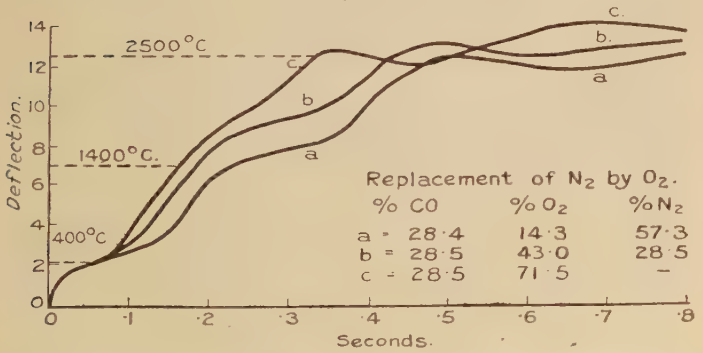


Fig. 7.



The decrease in dissociation is probably the most important factor causing the increased rapidity in the temperature rise.

The Effect of Hydrogen on CO-Air Mixtures.

The effect of the replacement by hydrogen of even so little as ·5 per cent. of the CO in the mixture $2CO + O_2 + 4N_2$

Fig. 8.

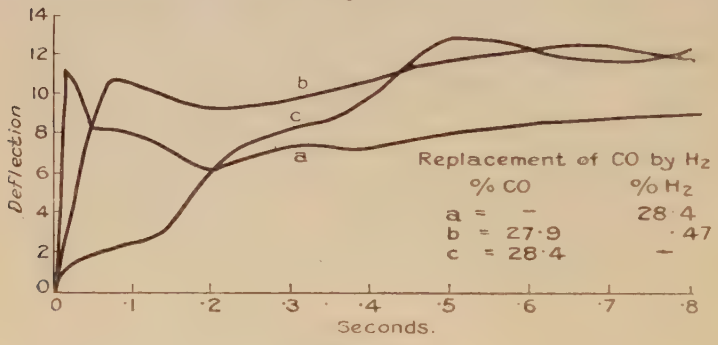


Fig. 9.

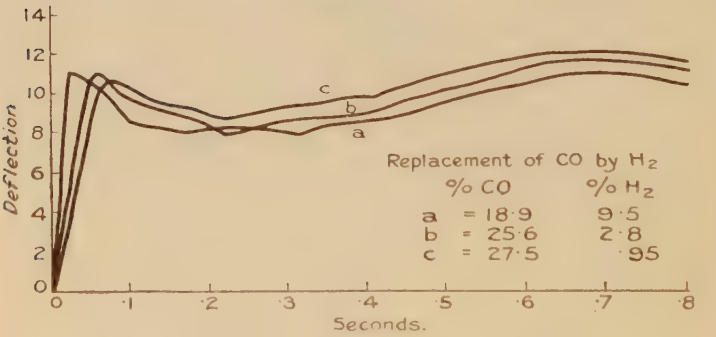
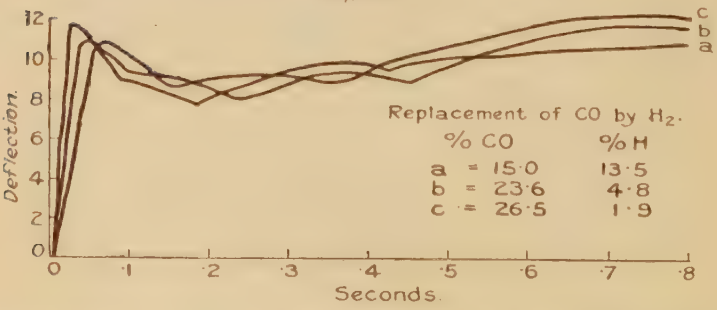


Fig. 10.



is completely to alter the whole shape of the curve. A rapid steady rise to about 2200° C. takes place, followed by a slight decrease in temperature. This is succeeded by a further rise to about 2500° C. The first rise takes place in ·08 second.

As more CO is replaced by H_2, the time of attainment of the first maximum decreases till, in the case of the $2H_2+O_2+4N_2$ mixture, the time is only ·01 second. The maximum temperature increases, and is highest in the case where the combustible gas approximates to water-gas.

The fall in temperature after reaching the maximum is much greater, and the subsequent rise much less, in those mixtures containing large percentages of H_2.

These results indicate the flame is spread principally by the agency of the hydrogen, but that in the mixtures weaker in H_2, some subsequent combustion of CO takes place.

The curves present other well-defined characteristics for which no satisfactory explanation can be assigned at present.

Some Theoretical Considerations of the Combustion of Carbon Monoxide.

The combustion of the most important simple combustible gases may be represented by the equations:

$$2H_2+O_2 = 2H_2O+68{\cdot}4 \text{ K.C.U./gm. mol.},$$

$$2CO+O_2 = 2CO_2+68{\cdot}0 \text{ K.C.U./gm. mol.}$$

These simple chemical equations might lead one to suppose that the two combustions were similar in nature; but even the most elementary observation makes it plain that there is a vast difference in the mechanisms of the two reactions. The characteristic colour and lambent nature of the flame of carbon monoxide contrasts strikingly with the faster-burning and almost colourless flame of hydrogen; while measurements of the velocity of the spread of flame in air-carbon-monoxide and air-hydrogen again emphasize this dissimilarity.

The peculiar colour of the carbon-monoxide flame has recently been investigated spectroscopically (Weston, Proc. Roy. Soc. 1925, pp. 1762 & 523), and the results are of great interest theoretically and will be referred to later.

One of the most remarkable facts about the carbon-monoxide combustion is the influence of water-vapour. Dixon stated that if the gas were dried as far as chemical methods will allow, it could not be caused to explode by an electric spark. These results, coupled with other discoveries about this time of the remarkable effect of traces of water-vapour on chemical change, led to the hypothesis that carbon monoxide cannot be directly oxidized, but only burns by virtue of the action of water-vapour.

Theories for the combustion of carbon monoxide through the introduction of water-vapour were put forward by several workers, who supposed that a series of compounds were formed during the combustion of the gas. The recent work of Professor Bone in this matter, coupled with our own experience, has, so far as we are concerned, settled the matter finally.

That Bone should have succeeded in exploding mixtures as dry as it is humanly possible to make them, merely by increasing the intensity of the spark-discharge, suggests that the difficulty is simply that of supplying sufficient energy, in a suitable form, to start the reaction.

The final and conclusive evidence, however, that carbon monoxide can burn without the assistance of steam, was produced by spectroscopic measurement.

The radiation from the flame of ordinary undried carbon monoxide burning in air consists of a large band extending a long way into the ultra-violet (Weston, Proc. Roy. Soc. 1925, pp. 176 & 523). In this radiation, however, the steam-bands can be clearly seen. When Bone exploded his dry gases and measured the radiation spectroscopically, the steam-bands, characteristic of the reaction involving water-vapour, were entirely absent. This remarkable evidence seems to prove beyond doubt that carbon monoxide can be oxidized directly in the absence of water-vapour.

The gases used in our present research contain certainly not more than three parts of water-vapour in 10,000, and we consider that at this concentration a large proportion of the carbon monoxide, at least, must be burned by direct oxidization.

The series of curves obtained for the rise in temperature over a very small volume of gas in the explosion sphere have all one remarkable characteristic, namely that they indicate three distinct stages in the explosion. These stages are absolutely characteristic of the combustion of carbon monoxide, and do not appear when other gases burning at a similar speed are used. We think that this indicates that the evolution of heat during the combustion of a molecule of carbon monoxide, is not the simple reaction of the combination of oxygen with the ionized gas, but is something rather more complex.

These curves are also what led us to think originally that the combustion of carbon monoxide was not the action of a few isolated water molecules, in turn, on a large number of carbon monoxide molecules, for if this were so, the reaction in the case of any particular carbonic oxide molecule, which

might be expressed

$$O_2 + 2CO + H_2O \longrightarrow [2CO \,.\, H_2O] + O_2 \longrightarrow 2CO_2 + H_2O,$$

would have to go to completion, involving the evolution of all the heat of combustion for this molecule, before the water became available for the combination of another carbonic oxide molecule.

In this case, considering the large number of molecules which directly affect the recording wire, the net result would be the steady evolution of heat, proceeding without break to the maximum temperature. It is only a theory which can allow for the combustion of all the molecules of carbon monoxide at nearly the same speed and time which will explain these results.

The theory which we put forward tentatively to explain this, involves the assignation of a definite electronic structure to carbon monoxide, and as this is an unsettled point we will deal with it first.

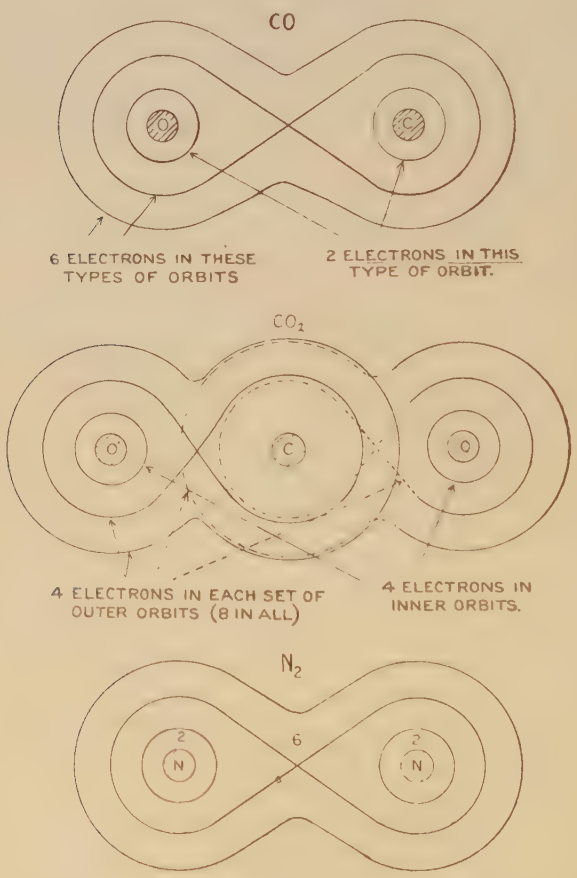
Carbon monoxide is, under ordinary conditions, a non-ionizable gas. In common with a large number of non-ionizable organic bodies and co-ordination compounds, it may be assumed that the atoms in carbon-monoxide are united by covalency. That is to say, they share a certain number of electrons. As to the exact orbital paths of those shared electrons, nothing has been proved, but for the purpose of this theory we shall assume that they circulate around both nuclei in the paths of the nature of the cassinian ovals, as was originally suggested by G. T. Morgan (Journal of the Chemical Society, vol. xliii. no. 44, pp. 1071–1073 (1924)).

We shall assume that in carbon monoxide the oxygen and carbon atoms are united by three covalent bonds, each of two electrons, and that of these six shared electrons four are provided by the oxygen atom and two by the carbon atom, leaving each nucleus the individual attentions of only two of its original valency electrons (see fig. 11). These six shared electrons all move in orbits of the cassinian type around both nuclei.

Since the combination of carbon and oxygen to form carbon monoxide involves the transfer of six electrons from the valency groupings to binuclear orbits, and also since carbon monoxide is formed with an evolution of heat, it must be assumed that the electrons in the binuclear orbits have less energy than those in uninuclear orbits. This is not an invariable rule, but in the case of compounds, such as carbon monoxide, methane, and other exothermic covalent substances, it appears to be true.

The molecule of carbon monoxide will normally be a fairly stable structure, but the effect of radiation of a suitable wavelength will be to drive the binuclear electrons into outer orbits, and when in this condition, the advent of a collision with an oxygen molecule will probably cause combination.

Fig. 11.



The exact mechanism of this combination is not yet known, though it is possible that a mathematical analysis of the spectrum of the explosion might yield detailed evidence as to the electronic movements.

It is probable, however, that the changes consist of several

progressive rearrangements, some of which will cause a large evolution of heat and others small absorptions of heat, and these will combine to give a temperature rise consisting of several stages. The final result, carbon dioxide, is still a covalent body, and its structure may be expressed as in fig. 11.

Here each oxygen atom is united to the carbon atom by two covalent bands, each of two electrons, and there are altogether eight binuclear electrons.

The remarkable fact about this combination is that, while it will proceed in the absence of water-vapour, the presence of water-vapour makes the reaction go much more readily.

Another fact of importance in the case of these dry mixtures has often been observed in these researches, namely that when firing by means of an electric spark, the mixture is often not ignited until the second and third spark. This is shown clearly on the results of the ionized-gap method (Burstall, Newey, and Crowe, Phil. Mag., June 1925, p. 1125) for flame-velocities, where the effect of a number of firing sparks can be observed.

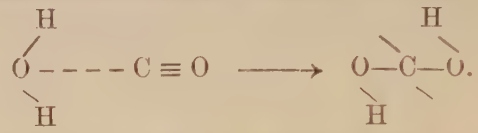
We consider that the action of the spark is to supply suitable radiation to the carbon monoxide molecules, driving some of the binuclear electrons into outer orbits—*i.e.*, to activate the molecules, and until a sufficient number of activated molecules are present, combustion cannot be started. In this respect the action of infra-red radiation on the combustion of carbon monoxide is interesting (W. T. David, Proc. Roy. Soc. Series A, vol. cviii. p. 617, 1925).

In this combustion water-vapour plays an important part. The molecules of carbon monoxide and water are probably associated in the gaseous state at ordinary temperatures.

It is possible, in the terms of the Co-ordination Theory, to arrange four atoms around one carbon atom. Thus a CO molecule will tend to attract a molecule of water into the co-ordination sphere, completely filling it and weakening the field between the carbon atom and the oxygen atom with which it is combined.

When the gas is ignited, binuclear electrons are driven, as already indicated, into outer orbits. The oxygen of the water molecule will readily capture one, causing a rearrangement

in the molecule of carbon monoxide, the valency of which now changes from co-valency to electro-valency.

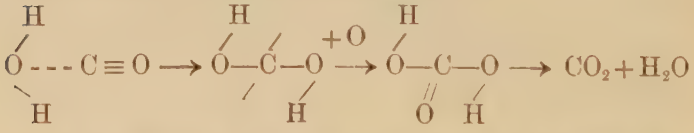


The di-hydroxy compound produced will be extremely active and unsaturated, since it will be easily seen that the C atom has two free valency electrons. These will be shared with the nearest free oxygen atom forming a molecule of carbonic acid.

At the temperature of the reaction this will be decomposed into one molecule of CO_2 and one of H_2O.

$$H_2CO_3 \longrightarrow CO_2 + H_2O.$$

The whole reaction may be represented



It is not supposed that the molecule of H_2O takes part in more than a few reactions; the molecules of CO which have no H_2O associated with them are oxidized directly. This will account for the quickening-up of the combustion, and also for the greater ease in ignition, due to the presence of water-vapour.

Owing to the probable similarity in structure of the molecules of nitrogen and carbon monoxide, the nitrogen possibly consisting of two nuclei united by three covalent bonds as shown in the figure, it seems that nitrogen should be able to absorb the radiation emitted by burning carbon monoxide, producing a certain instability of the nitrogen molecule which may result in its being directly oxidized.

That this takes place at high pressures has been demonstrated by Bone (Bone, Newitt, and Townsend), and our own results in the replacement of the nitrogen in the mixture

$$2CO + O_2 + 4N_2$$

by carbon monoxide and by oxygen show that it is probably taking place at initial pressures of 105 cm. The exhaust gases in a theoretical carbon-monoxide air mixture at 105 cm.

initial pressure contained 2 per cent. of oxides of nitrogen, The method of analysis was to use a large volume of gas, absorb the oxides of nitrogen in dilute caustic soda solution, and estimate them by the phenol sulphonic acid method. It is hoped that further investigation will clear up this point.

The experiments carried out with mixtures containing small quantities of hydrogen confirm the results of a number of other workers, most of whom have used some sort of pressure indicator as a means of determining rapidity of combustion. As we have used a new method of investigation, the curves are very interesting, and they indicate that there is a considerable amount of after-burning in the case of those mixtures containing only small quantities of hydrogen. In the case where hydrogen and carbon monoxide are present in equal quantities, the burning appears to be almost identical with that of pure hydrogen, the small after-rise being accounted for by the adiabatic compression of the gas by the burning of the remainder of the charge.

In the mixtures containing less hydrogen the later portions of the curves indicate that the carbon monoxide is not all burned in the initial spread of flame, and that some after-combustion takes place. In the water-gas mixture the burning is probably represented by

$$2H_2+O_2 = 2H_2O,$$
$$2H_2O+2CO \rightleftharpoons 2CO_2+2H_2,$$
$$2H_2+O_2 = 2H_2O, \text{ etc.};$$

but in the other cases it is very much more difficult to decide, and we think that it is probable that some of the CO present is burning by direct oxidation. It is hoped that determinations of actual flame-velocities will help to clear up this point.

Summary and Conclusions.

A method of investigating flame velocities at constant volume in a sphere by means of resistance thermometers and an Einthoven Galvanometer is described.

A means of using this combination to obtain an insight into the nature of the chemical reactions taking place is also described.

The explosion $2CO_2+O_2 = 2CO_2$ with varying diluents and impurities has been investigated at 105 cm. initial pressure, and the following results arrived at :—

(1) The combustion of carbon monoxide takes place in two ways :

(*a*) Direct oxidation to CO_2.

(*b*) Oxidation by the intervention of water.

In the second case, ignition is easier and the flame-speed much higher. Under ordinary conditions both reactions occur simultaneously.

(2) The replacement of the nitrogen diluent by oxygen or carbon monoxide produced a considerable acceleration in both the velocity of combustion and in the velocity of flame-spread. The effect of carbon monoxide as a diluent is much greater than that of oxygen in accelerating the combustion; but whether this is entirely due to the dissociation effect or to the possible activation of nitrogen is not yet clear.

(3) The presence of extremely small traces of hydrogen in the mixture produced effects out of all proportion with the amount of hydrogen present. As little as one-half per cent. of hydrogen completely alters the process of combustion of the carbon-monoxide air-mixture.

(4) The method gives an accurate way of measuring the spread of flame from point to point in a spherical or other closed vessel. In addition to this, it can be used to measure the way in which temperature rises at a point in the explosion chamber, although an accurate value for temperature cannot of course be obtained.

The authors wish to express their indebtedness to the Government Department of Scientific and Industrial Research for grants which have enabled two of them to devote their full time to this research.

TABLE I.

Variation of Mixture Strength for CO and Air-mixtures.

Number of Experiment.	Percentage of CO.	Percentage of Air.	Initial Pressure.	Initial Temperature	Figure.
7	20·1	79·9	94·2 cm. Hg.	10·8 C.	2 *a*
9	25·0	75·0	100·9 „	13·5 C.	2 *b*
11	28·4	71·6	105·6 „	14·4 C.	3 *a*
12	34·5	65·5	116·4 „	13·0 C.	2 *c*
14	39·6	60·4	126·3 „	17·0 C.	3 *b*
17	44·6	55·4	136·8 „	17·3 C.	4 *a*
18	49·8	50·2	151·0 „	17·8 C.	3 *c*
23	55·9	44·1	164·7 „	13·6 C.	4 *b*
25	60·0	40·0	187·6 „	15·4 C.	4 *c*

The partial pressure of air in all the above mixtures is approximately the same, viz. about 75 cm. mercury.

TABLE II.

Variation of Mixture Strength for CO and Oxygen.

Number of Experiment.	Percentage of Co.	Percentage of Oxygen.	Initial Pressure.	Initial Temperature.	Figure.
29	20·9	79·1	95·0 cm. Hg.	11·5 C.	5 *a*
31	24·9	75·1	100·0 „	14·7 C.	5 *b*
32	28·6	71·4	104·5 „	15·0 C.	5 *c*

TABLE III.

Effect of Replacement of N_2 by O_2 and CO in $2CO_2+O_2+4N_2$.

Number of Experiment.	Percentage of CO.	Percentage of Oxygen.	Percentage of Nitrogen.	Initial Pressure.	Initial Temperature.	Figure.
57	28·4	14·3	57·3	106·1 cm. Hg.	19·4 C.	7 *a*
62	28·5	43·0	28·5	105·1 „	18·1 C.	7 *b*
63	28·5	71·5	—	105·1 „	17·0 C.	7 *c*
71	28·5	14·3	57·2	105·0 „	18·0 C.	6 *a*
72	57·0	14·3	28·7	105·0 „	13·0 C.	6 *b*
73	85·6	14·3	—	105·0 „	18·5 C.	6 *c*

TABLE IV.

Effect of Replacement of CO by H_2 in $2CO+O_2+4N_2$.

Number of Experiment.	Percentage of CO.	Percentage of H_2.	Percentage of Air.	Initial Pressure.	Initial Temperature.	Figure.
45	—	28·4	71·6	105·7 cm. Hg.	16·7 C.	8 *a*
49	27·9	·47	71·63	106·2 „	19·9 C.	8 *b*
57	28·4	—	71·6	106·1 „	19·4 C.	8 *c*
50	18·9	9·5	71·6	106·0 „	21·2 C.	9 *a*
48	25·6	2·8	71·6	106·1 „	22·0 C.	9 *b*
47	27·5	·95	71·55	106·1 „	20·3 C.	9 *c*
53	15·0	13·5	71·5	106·7 „	17·2 C.	10 *a*
46	23·6	4·8	71·6	106·1 „	19·5 C.	10 *b*
51	26·5	1·9	71·6	106·1 „	22·0 C.	10 *c*

TABLE V.

Determination of Flame-velocities.

Number of Experiment.	% CO.	$\%O_2$.	$\%N_2$.	% Moisture.	Mean Flame-velocities. 1st Half.	2nd Half.
81	28·5	14·3	57·2	Dried over $CaCl_2$.	76·0 cm./sec.	58·5 cm./sec.
82	85·5	14·5	—	„	173·0 cm./sec.	140·0 cm./sec.
84	28·6	71·4	—	„	127·0 cm./sec.	108·0 cm./sec.
87	28·1	13·9	55·6	2·5	148·0 cm./sec.	129·0 cm./sec.

Number of Experiment.	% CO.	$\%H_2$.	% Air.	% Moisture.	Mean Flame-velocity.
108.....	27·5	·95	71·6	Dried over $CaCl_2$.	640 cm./sec.

V. *On the Theory of Earth-Currents Measurement.* *By* A. PETROWSKY *.

CONTENTS.

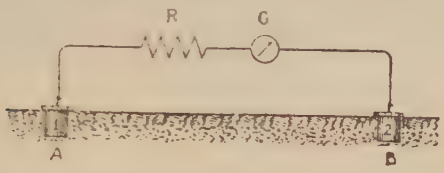
§ 1. Stating the problem.
§ 2. Differential equations and boundary conditions of work of the electrode in a limitless medium.
§ 3. Discovery of a common integral for the electric potential.
§ 4. Values of arbitrary constants.
§ 5. Effect produced on the value of the electric potential by a plane surface bordering the medium.
§ 6. Potential for the semi-sunk electrode.
§ 7. Distribution of isopotential surfaces and of lines of force under various conditions.

§ 1. FOR measuring the earth currents a pair of non-polarizing electrodes are introduced into earth, connected to each other through a sensitive galvanometer G (fig. 1) by means of a conductor. A portion of the earth-current branches off into the latter, all neighbouring current-lines being subjected to more or less considerable changes.

* Communicated by the Author.

To obtain a correct idea of the quantities characteristic of the electric field, the deflexion of the galvanometer must be taken with due estimation of the above-mentioned changes.

Fig. 1.—Scheme of earth-currents measurement.



The present paper deals with such estimation, the following propositions being made :—

(1) The field under consideration is homogeneous and is being observed in a uniform isotropic limitless medium.
(2) The electrodes are spherical in shape.
(3) The specific conductivity of the substance of the electrode is many times higher than that of the environing medium.
(4) The distance between the electrodes is very considerable in comparison with their size.

§ 2. Let the right-hand system of polar coordinates be disposed in such a manner as to make the axis OX pass through the centre of the sphere bordering the surface of the electrode, and to be directed along the lines of force of the homogeneous electric field under consideration (fig. 2). In such a case, the system being symmetrical in regard to that axis, we may consider the electric potential U as well as all other values as functions of only two variables, the radius r and the polar angle θ :

$$U = U(r, \theta).$$

The value U must satisfy the differential equation of Laplace, which for the considered case takes the form

$$\frac{\partial^2 U}{\partial r^2} + \frac{2}{r}\frac{\partial U}{\partial r} + \frac{1}{r^2}\frac{\partial^2 U}{\partial \theta^2} + \frac{\cot\theta}{r^2}\frac{\partial U}{\partial \theta} = 0. \quad . \quad . \quad (1)$$

Moreover, this function U must be finite, single-valued, and continuous, and must satisfy the following conditions :

(*a*) For the surface of the electrode, the electric potential must have a certain constant value U_1 ; consequently

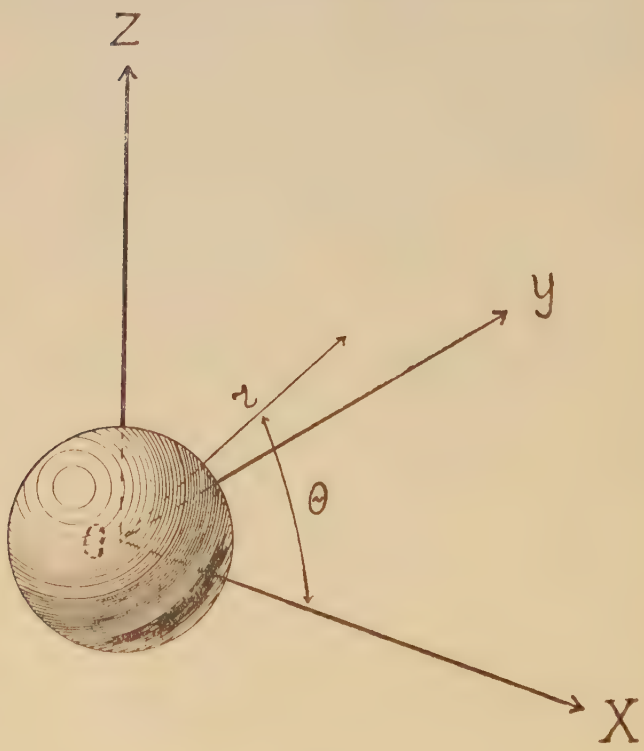
$$r = r_0, \quad U = U_1. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(*b*) For any very distant point of the space the electric potential must keep the value it had before the electrode was sunk and, consequently, must be expressed by the function

$$r=\infty, \quad U_\infty = U_0 - F(x-x_1) = U_0 - Fr\cos\theta \quad . \quad (3)$$

where x_1 is the coordinate of the centre of the electrode, U_0 and F constant numbers given.

Fig. 2.—A spherical electrode in a uniform medium.



§ 3. The solution of this differential equation is sought in the form

$$U(r, \theta) = U'(r)\cos\theta + U''(r), \quad . \quad . \quad . \quad (4)$$

where $U'(r)$ and $U''(r)$ are functions of the radius r only.

Differentiating the expression (4) and introducing in the equation (1) we obtain

$$\left(\frac{d^2U'}{dr^2}+\frac{2}{r}\frac{dU'}{dr}-\frac{2}{r^2}U'\right)\cos\theta+\frac{d^2U''}{dr^2}+\frac{2}{r}\frac{dU''}{dr}=0, \quad (1')$$

which divides into two common differential equations:

$$\frac{d^2U'}{dr^2}+\frac{2}{r}\frac{dU'}{dr}-\frac{2}{r^2}U'=0, \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{d^2U''}{dr^2}+\frac{2}{r}\frac{dU''}{dr}=0. \quad . \quad . \quad . \quad . \quad (6)$$

Integrating the differential equations (5) and (6), and taking the sum of integrals, we obtain the entire expression for the potential sought in the form

$$U=\left(Ar+\frac{B}{r^2}\right)\cos\theta+\frac{C}{r}+D. \quad . \quad . \quad . \quad (7)$$

§ 4. The arbitrary constants A, B, C and D are found according to the above boundary conditions, namely:

(*a*) Substituting in the expression (7) $r=\infty$, we obtain

$$U_\infty=A(x-x_1)+D, \quad . \quad . \quad . \quad . \quad . \quad (3')$$

which on identification with the boundary condition (3) gives

$$A=-F, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$D=U_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

(*b*) Substituting in the expression (7) $r=r_0$ and taking into consideration (8) and (9), we obtain

$$U_1=\left(-Fr_0+\frac{B}{r_0^2}\right)\cos\theta+\frac{C}{r_0}+U_0, \quad . \quad . \quad . \quad (2')$$

which on identification with the boundary condition (2) gives

$$B=Fr_0^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$C=-(U_0-U_1)r_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

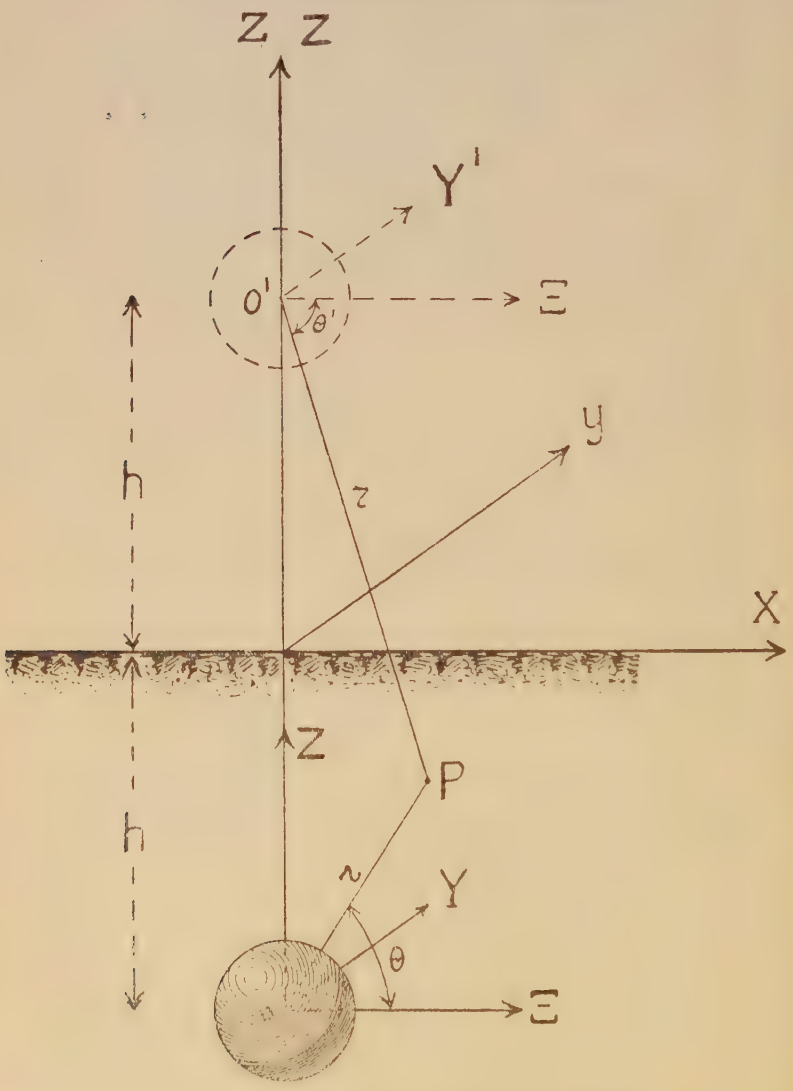
It follows from the above that the final expression for the electric potential is

$$U=U_0-\frac{(U_0-U_1)r_0}{r}-Fr\left(1-\frac{r_0^3}{r^3}\right)\cos\theta. \quad . \quad (12)$$

§ 5. We have assumed till now that the electrode is placed in a limitless medium. However, in reality its centre is at a

certain depth h under the earth's surface (in particular cases h can be equal to zero). The specific conductivity of the

Fig. 3.—An electrode and its electric image.



air being insignificant in comparison with that of the soil, the current-lines when reaching the earth's surface are

forced to turn horizontally. This introduces a new alteration in the electric field, which is felt in all other points of the same.

Mathematically it leads to the fact that, but for two boundary conditions expressed under § 2, the potential must further satisfy a third condition, namely, for

$$Z=h, \quad \frac{\partial U}{\partial Z}=0. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The solution of the question may be approached as follows. Let it be supposed :

(*a*) That on the same vertical as the electrode, and at the same distance from the earth's surface, but above the latter, another identical sphere is placed (fig. 3) ;

(*b*) that the separating surface exists no longer, and the whole of the limitless space is filled with the same medium as that environing the electrode ;

(*c*) that in the upper zone of the space (above the former separating surface) there is another homogeneous field like that in the lower zone ;

(*d*) that the potential of the upper sphere is likewise constant and equal to U_1.

To be brief, let us fancy a mirror image of the given electrode (the true image, viz. without changing the sign of the potential). This mirror image will produce at all points of the space the electric potential u, which is expressed through the same function (7) as above, with the difference that for r must be substituted r' (the distance of the considered point to the centre of the image), and for the angle θ the angle θ'. We have, consequently,

$$u=\left(Ar'+\frac{B}{r'^2}\right)\cos\theta'+\frac{C}{r'}+D. \quad . \quad . \quad . \quad (7')$$

The entire potential W produced in any point by all the causes will be equal to the sum of potentials produced by both spheres.

$$W=U+u=\left(Ar+\frac{B}{r^2}\right)\cos\theta+\frac{C}{r}+D$$

$$+\left(Ar'+\frac{B}{r'^2}\right)\cos\theta'+\frac{C}{r'}+D; \quad (14)$$

or in the coordinates of Descartes,

$$W=\left(A+\frac{B}{[(x-x_1)^2+y^2+z^2]^{\frac{3}{2}}}\right)(x-x_1)$$
$$+\frac{C}{[(x-x_1)^2+y^2+z^2]^{\frac{1}{2}}}+D$$
$$+\left(A+\frac{B}{[(x-x_1)^2+y^2+(z-2h)^2]^{\frac{3}{2}}}\right)(x-x_1)$$
$$+\frac{C}{[(x-x_1)^2+y^2+(z-2h)^2]^{\frac{1}{2}}}+D. \quad . \quad (14')$$

The same function must express the potential produced by one electrode on placing it in a uniform isotropic medium, limitless on one side and bordered on the other by a plane at distance h from its centre.

§ 6. The expression obtained presents a single-valued, finite, and continuous function of coordinates ; moreover, it is easy to see that it gives on the former separating surface, viz. for $z=h$, only the tangential component of the electric force. There remains only to choose the arbitrary constants A, B, C, and D in such manner as to again satisfy the conditions (a) and (b).

Suppose that in the expression (14) $r=\infty$, $r'=\infty$. We write

$$W_\infty=A(x-x_1)+D+A(x-x_1)+D,$$

and identifying it with the boundary condition (3) find that

$$A=-\frac{F}{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$D=\frac{U_0}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It remains to satisfy the second boundary condition (2), which may be done either approximately, if the electrode is sunk deeply $\left(\frac{h}{r_0}>10\right)$, or with precision, if the centre of the electrode lies on the separating surface itself (fig. 4). Such semi-sunk electrode has $h=0$, and the mirror image is coinciding with the electrode, the following equations

holding:

$$\left.\begin{aligned} r' &= r, \\ \theta' &= \theta, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

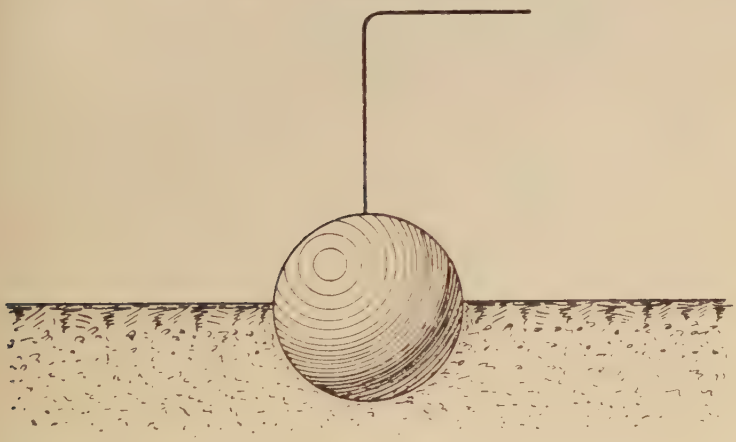
from which it also follows that

$$W = 2U = 2\left(Ar + \frac{B}{r^2}\right)\cos\theta + 2\left(\frac{C}{r} + D\right). \quad . \quad (18)$$

Substituting in this expression $r = r_0$, $W = U_1$, we obtain

$$U_1 = 2\left(Ar_0 + \frac{B}{r_0^2}\right)\cos\theta + 2\left(\frac{C}{r_0} + D\right). \quad . \quad (2'')$$

Fig. 4.—Semi-sunk electrode.



This equation may be satisfied identically, supposing

$$B = -Ar_0^3 = \frac{Fr_0^3}{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$C = \frac{(U_1 - 2D)r_0}{2} = -\frac{(U_0 - U_1)r_0}{2}. \quad . \quad . \quad (20)$$

The final expression for the electric potential is

$$W = U_0 - \frac{(U_0 - U_1)r_0}{r} - F\left(1 - \frac{r_0^3}{r^3}\right)\cos\theta. \quad . \quad (21)$$

§ 7. The figures 5–10 show the electric field on the separating surface for the case of a semi-sunk electrode.

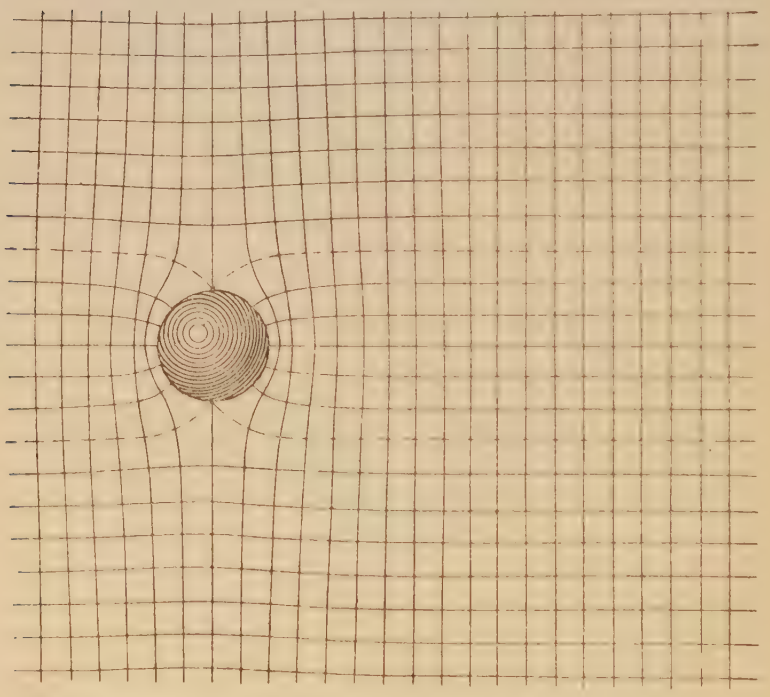
The diagrams are constructed according to the following data :—

Radius of the electrode, $r_0 = 5$ cm.

Initial potential in the plane passing through the centre of the electrode, $U_0 = 10$ V.

Initial electric force of the homogeneous electric field, $F = 0{\cdot}2 \frac{V}{cm.}$.

Fig. 5.—Electric field near the electrode. Circuit open.



The potential of the electrode during work is taken as equal to

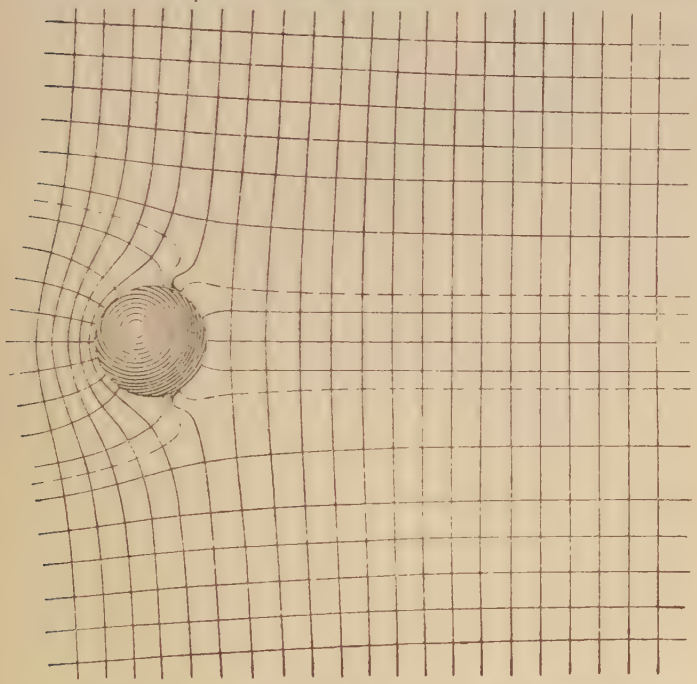
(*a*) In fig. 5, $U_1 = 10{\cdot}0$ V ; $\theta = 90°$.
(*b*) „ „ 6, $U_1 = 8{\cdot}50$ V ; $\theta = 60°$.
(*c*) „ „ 7, $U_1 = 7{\cdot}90$ V ; $\theta = 45°$.
(*d*) „ „ 8, $U_1 = 7{\cdot}42$ V ; $\theta = 30°$.
(*e*) „ „ 9, $U_1 = 7{\cdot}00$ V ; $\theta = 0°$.
(*f*) „ „ 10, $U_1 = 0{\cdot}00$ V ;

The examination of these figures shows as follows :—

(*a*) The sinking of the electrode into the soil produces an alteration in the electric field. If the potential of the electrode remains during work equal to the initial value of

U_0, the electrode moves asunder the isopotential surfaces disposing them symmetrically on both its sides. At the same time, the lines of force curve in the proximity of the electrode, enter into the latter, come out of it and then run towards the second electrode. The alteration of the field takes place within the limits of the triple area of the active cross-section of the electrode. The other lines of force

Fig. 6.—Electric field near the electrode. Circuit closed for very high resistance.



curve gently, forming a depression on the traverse of the electrode, and then reassume their former direction. At a very small distance (about the double radius, counting from the centre) from the electrode, the electric field almost entirely conserves its uniformity.

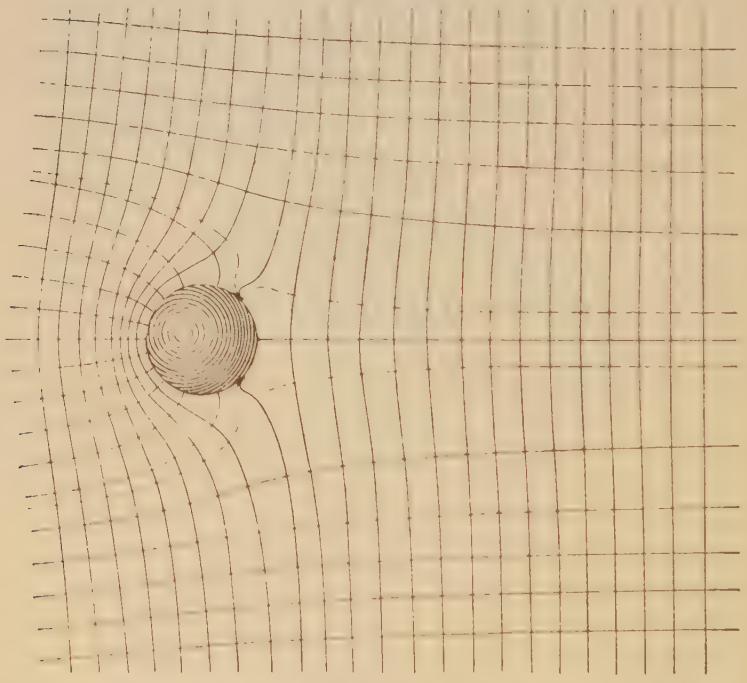
The dotted line shows the boundaries of the zones the space is divided into : zone of capturing, zone of transgressing, and zone of skirting force lines (and current also).

(*b*) If the potential of the electrode diminishes during work, which occurs during the use of the current, the symmetry is broken, the isopotential lines of the field curve more strongly on the entrance side and embrace the electrode so as to communicate to the latter the direction towards the

second electrode. At the same time the zone of distortion of the field grows, and the force-current entering into the electrode proves unequal to that coming out of it. The curve of the lines turning round the electrode occurs not on the traverse of the centre, but in the interval between two electrodes.

The limit case of the described changes is shown in fig. 9, where the force-current gathered from a twelve-fold area enters through the whole surface of the electrode, the

Fig. 7.—Electric field near the electrode. Circuit closed for high resistance.



leaving lines of force are totally lacking, whereas the whole interval between the electrodes is filled with lines turning the electrode from the side. The distortion of the field remains noticeable at a distance of about four degrees from the centre of the electrode.

(*c*) During further change of the potential the space environing the electrode divides yet in two zones—that of capturing and that of circuition. In the former, the lines of force curving more or less sharply enter into the electrode from all the sides ; the lines of force of the latter zone turn

Fig. 8.—Electric field near the electrode. Circuit closed for not high resistance.

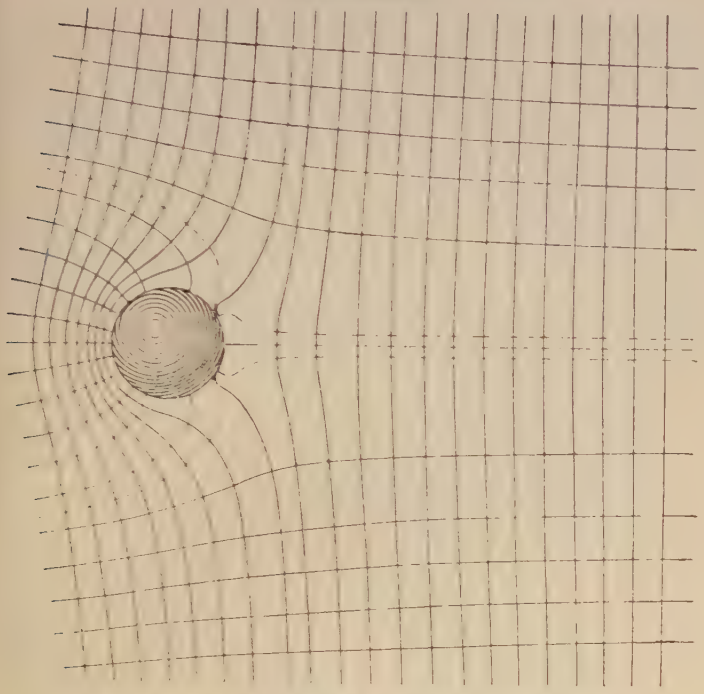
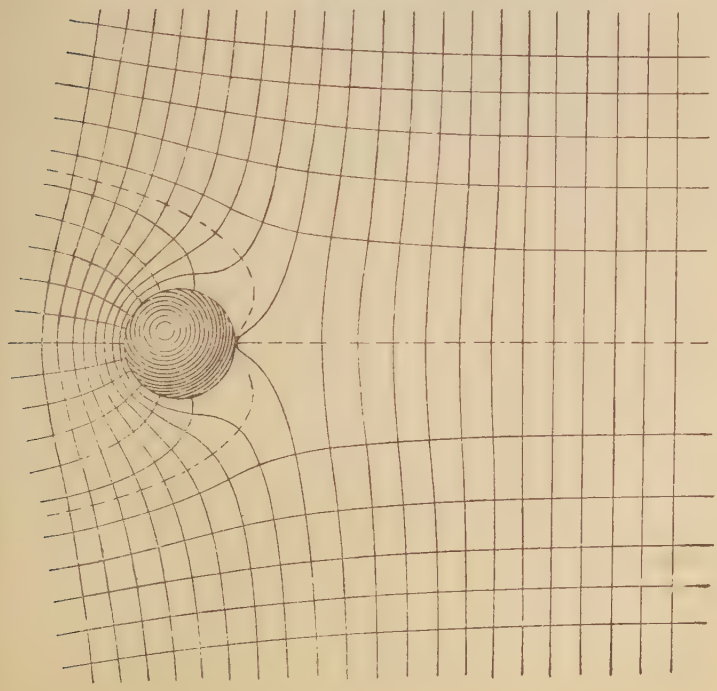


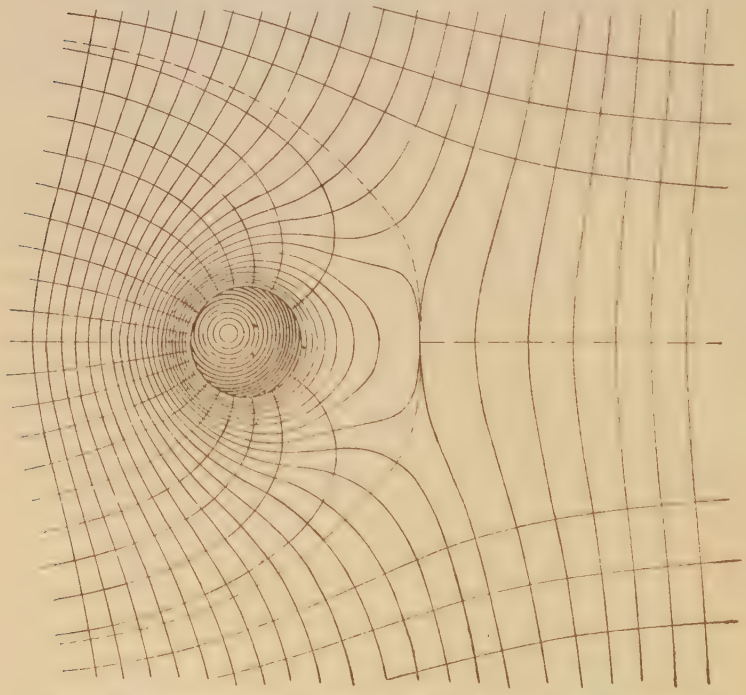
Fig. 9.—Electric field near the electrode. Circuit closed for low resistance.



round the electrode and, declining from the straight direction, fill, though with lesser density, the whole space between the electrodes ; the limits of the distortion of the field grow much wider, and depend not only on the size of the electrode but on the distance between the two electrodes.

When the distance between the electrodes is considerable we may accept, to a sufficient approximation, that the changes in the electric field, occurring about the first electrode, are repeated near the second, but all the curves of the isopotential surfaces and of lines of force are directed inversely.

Fig. 10.—Electric field near the electrode. Short circuit.



Thus the constructed theory gives us the full picture of the distortions provoked in the considered field by the sinking of electrodes into the soil. Using the expression found for the electric potential, there is no difficulty in making an estimation of all these alterations and introducing proper corrections, as well as exact calculations of elements characteristic of the field, according to the results of the experiment.

VI. *Note on the Electrostatic Charge on Glass Floats in Very Dry Liquids.* *By* Prof. H. V. A. Briscoe, *D.Sc., A.R.C.S., F.I.C.*, P. L. Robinson, *D.Sc., F.I.C., and* H. C. Smith, *M.Sc.**

THE phenomena here described occurred in silicon tetrachloride and in boron trichloride, which had been carefully purified for atomic weight determinations. This purification of the silicon tetrachloride was effected, both chemically and by repeated fractional distillation in dry air and finally *in vacuo*, in a manner described in detail by two of us in a recent paper (Robinson and Smith, Journ. Chem. Soc. cxxviii. p. 1262. 1829). The boron trichloride was purified in a similar rigorous manner for use in a like investigation (Briscoe and Robinson, *ibid.* cxxvii. p. 696, 1925).

As it was intended to make precise determinations of the density and thermal expansion of silicon tetrachloride by observation of the flotation-temperatures of calibrated glass floats, the liquid was distilled *in vacuo* into specially cleaned and dried cylindrical Durosil glass vessels 3 cm. in diameter and containing two floats which were about 3 cm. by 0·5 cm. During the distillation the receivers were cooled in liquid air, and when they contained enough material to fill them to a depth of 11 cm. with liquid, they were sealed off from the train while most of the distillate was still solid. When this solid was allowed to melt without disturbance, the floats moved freely up and down in the liquid as the temperature varied and as the liquid consequently changed its density. But a very slight agitation, even that involved in merely laying the vessel on its side two or three times, was sufficient to cause the floats to attach themselves to the sides of the vessel so firmly that they could only be dislodged by very vigorous shaking, and then, immediately, they stuck fast at another point. Even the slightest tremor produced in the liquid by a small electric motor running on the same bench sufficed to prevent the floats from moving freely.

The whole behaviour of the floats was consistent with the view that they had acquired electric charges, presumably by friction between glass and liquid. As two floats in the same vessel both stuck to the sides, but when freed repelled each other, it appeared that the floats had similar charges. When a glass rod previously rubbed with dry silk was presented to the vessel, the floats were repelled. Hence they were positively charged. Furthermore, after a float had been stuck

* Communicated by the Authors

for some time to a particular spot on the surface of the container, it tended, when shaken free, to return to the same area, which, evidently, had acquired and retained an induced charge opposite in polarity to that of the float.

When the vessel was left undisturbed for some time, the floats eventually lost the greater part of their charge and moved quite freely, so that the desired observation of flotation-temperatures could be made with precision. It was observed, however, that the floats never lost entirely the tendency to be repelled by a positively-charged object, and it seems probable that a very slight charge, insufficient to hinder the movements of the floats, was maintained by the slight vibration of the building.

With the lapse of time after the distillation of the liquid it was found that (*a*) the tendency of the floats to acquire a charge diminishes, and (*b*) the period required for the dissipation of the charge on the floats, *i. e.* so far as to render them free-moving, fell markedly from 5–7 days originally to under 2 days after a period of eight weeks. These observations suggest that the conductivity of the liquid increased with time, and it is evident that this may be explained if we suppose the liquid to have a slight but slowly progressive action on the glass.

The behaviour of the floats in boron trichloride was of a similar character, but much less striking and inconvenient. The charges were found in each case after shaking, boiling, or bumping had occurred, or when the vessel was agitated a long time. They were positive in sign, as shown by the repulsion exercised by a charged glass rod, but were very much smaller in magnitude. There was no sticking to the glass, even in the worst case. When produced the charges were readily dissipated, being sufficiently diminished for float work in two hours at the most, and appeared to be completely lost after a day; whereas in the case of silicon tetrachloride slight charges remained even after four months.

The writers desire to thank Prof. W. M. Thornton for his kindly interest in these phenomena, and for helpful suggestions as to their further investigation.

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VII. *Forced Oscillations in a Circuit with non-linear Resistance. (Reception with reactive Triode.)* *By* BALTH. VAN DER POL, Jun., *D.Sc.**

§ 1. *Introduction.*

WHEN an E.M.F. $B \sin \omega t$ acts on a circuit consisting of a self-inductance L, capacity C, and ohmic resistance r, free and forced oscillations are generally set up, the amplitude b of the forced oscillation being given by

$$b = \frac{B}{\sqrt{\left(L\omega - \frac{1}{C\omega}\right)^2 + r^2}}.$$

Should the system, in addition, be in resonance with the external E.M.F. so that

$$L\omega - \frac{1}{C\omega} = 0,$$

the resultant amplitude would have the value

$$b = \frac{B}{r}.$$

It follows from this that when r approaches zero value, the amplitude b would become infinite.

A circuit electrically coupled to a triode with reaction may be regarded as a system the resistance of which varies with the reaction, the resistance being positive when the reaction coupling is loose. The circuit will commence to oscillate, however, when the point of critical reaction is passed and would then act as if the resistance were negative. At the critical value of the reaction the resistance is zero. (The term resistance here denotes what might conveniently be called the "differential resistance" as defined by $\frac{dV}{di}$, which expression has the dimension of a resistance analogous to $\frac{V}{i}$).

According to the above elementary consideration, should the critical point of the reaction be approached, even the least external E.M.F., tuned to the frequency of the circuit,

* Communicated by the Author. This paper was first published in the Dutch language (1924) in *Tijdschr. van het Nederlandsch Radiogenootschap*, October 1924.

would set up forced oscillations, the amplitude of which would tend to increase to infinity. This is of course contrary to actual experience.

The bends of the characteristics of the triode limit in practice the resultant amplitude. We are therefore forced to consider the resistance of the circuit as being dependent on the existing amplitude.

The deduction of this non-linear resistance from the triode characteristics has already been fully shown in previous publications * and need not be further gone into at present. If the coupling is increased past the critical reaction coupling, the resistance becomes negative and, considered linearly, the amplitude of the forced oscillation should commence to decrease again in accordance with the equation:

$$b = \frac{B}{\sqrt{(-r)^2}} = \frac{B}{r}.$$

Linearly considered, therefore, a negative resistance would not impart greater signal strength than a positive resistance of equal magnitude, and in order to obtain maximum signal strength it would apparently only be necessary to reduce the resistance to a minimum.

The free oscillations, however, which automatically fade away in the case of a positive resistance, increase exponentially when the resistance is negative. The interference of the free oscillations would become apparent for the first time at the moment the resistance becomes zero.

The experiments by Vincent, Möller, Miss Leishon, Mercier, Rossman and Zenneck †, which are fully confirmed by accurate observations made on wireless reception using a reactive triode, show, on the contrary, that a circuit *does not* oscillate spontaneously when the reaction passes the critical point of a triode system, when the latter is tuned for the reception of signals.

It can be demonstrated especially in the case of wireless telephonic reception of a carrier wave, that the reaction may be brought past the critical point without spontaneous free oscillations being set up in the circuit, which is under the influence of the carrier wave. As soon as the influence of

* Van der Pol, *Tijdschr. v. h. Ned. Radiogen.* i. p. 1 (1920). Van der Pol, Radio Review, i. p. 701 (1920). Appleton and Van der Pol, Phil. Mag. xlii. p. 201 (1921).

† Vincent, Proc. Phys. Soc. Lond. xxxii. p. 84 (1920). Möller, *Jahrb. f. drahtl. Tel.* xvii. p. 269 (1921). Miss Leishon, Phil. Mag. xlvi. p. 686 (1923). Mercier, *C. R.* clxxiv. p. 448 (1922). Zenneck, *Jahrb. f. drahtl. Tel.* xxiii. p. 47 (1924).

the carrier wave ceases, the circuit commences to generate free oscillations. This phenomenon may also be observed in the following simple way.

A receiving circuit will oscillate spontaneously when detuned during the reception of a carrier wave, or during telephonic reception, when the reaction coupling is greater than the critical. This is proved by the production of an audible combination tone built up by the detection (quadratic terms) from the free and forced oscillations.

If the tuning is now brought closer to resonance, the combination tone will become lower and then suddenly disappear, though the frequency still differs from zero. The combination tone is therefore not heard close to the point of resonance. This is not due to the frequency being too low to be heard, but to the actual disappearance of this beat note, caused by the *absence of free oscillations,* forced oscillations only being present in the circuit.

The explanation of this essentially non-linear phenomenon must be sought in the fact that the representative point passes at a given period through a section of the triode-characteristic where it encounters a smaller slope, so that the resistance is no longer negative but positive. This occurs with forced oscillations when the reaction coupling is greater than the critical. The effective influence is that the free oscillation is discouraged to build up, for, what might conveniently be termed "the remaining average resistance," may under these circumstances no longer be negative.

This *suppression of the free by the forced oscillations* must be ascribed to the interaction of both types of oscillation *. This interaction is entirely absent in linear circuits but is, as has already been explained elsewhere, of vital importance in the production of triode oscillations. There can be no question here of the free oscillations being "taken along by" the forced oscillation, as is sometimes expressed in articles on this subject, although in passing we may as well point out that the presence of forced oscillations renders the free oscillations subject to a frequency-correction, which behaves as if the forced "attracted" the free frequency.

Six years ago the problem of forced oscillations in a circuit with non-linear resistance was investigated for the first time by the author †. The differential equation

$$\ddot{v} + \phi(v)\dot{v} + \omega_0^2 v = \omega_1^2 \mathrm{B} \sin \omega_1 t,$$

* The synchronous time-keeping of two clocks hung on the same wall, as long ago observed by Huygens, is another example of the suppression of free by forced oscillations.

† Van der Pol, *Tijdschr. v. h. Ned. Radiogen.* i. p. 1 (1920).

deduced at the time, again forms the basis of the present investigation. Our remarks, however, were then confined solely to dealing with the case where the resistance remained positive. At a later date and in collaboration with Dr. Appleton, the general theoretical problem where the resistance could also be negative was investigated, the results of which are to be found in an article by Dr. Appleton *. The present article, however, is more general and gives a more detailed account of the experiments.

In conclusion it should be pointed out that, although the conception of free and forced oscillations is essentially linear, this interpretation has been adhered to in the present non-linear investigation in view of the fact that, when the logarithmic increments or decrements are small, as is generally the case, the resistance-correction of the frequency would be negligible and the non-linear resistance characteristic would merely find expression as a first approximation in limiting the amplitudes.

§ 2. The differential equation for the anode voltage of a triode receiver acted upon by an external periodic E.M.F. is expressed by

$$\ddot{v}+\phi(v)\dot{v}+\omega_0^2 v=\omega_1^2 \mathrm{B}\sin\omega_1 t, \quad . \quad . \quad . \quad (1)$$

in which B denotes the amplitude of the external E.M.F., due for example to a signal, $\omega_0^2=\frac{1}{\mathrm{CL}}$ the square of the angular frequency of the receiver, and ω_1 the angular frequency of the external E.M.F.

Furthermore,

$$\int\phi(v)dv=\frac{rv}{\mathrm{L}}+\frac{\psi(v)}{\mathrm{C}},$$

in which r denotes the ohmic resistance of the L, C, r circuit, and $\psi(v)$ the "oscillation characteristic" † of the reactive triode.

Eliminating all secondary considerations having no direct bearing on the present investigation, the problem resolves itself into the study of an electric disturbance in a circuit as indicated in fig. 1.

To simplify matters it is assumed that the triode is adjusted to work on a symmetrical portion of the oscillation characteristic, such that no even terms ‡ occur in the powers

* Appleton, Proc. Cambr. Phil. Soc. xxiii. p. 231 (1923).

† Appleton and Van der Pol, Phil. Mag. xliii. p. 179 (1921).

‡ The quadratic term βv^2 is of no importance in the first approximation, when considering the amplitudes. The principal influence of the term βv^2 is found in detection and modulation.

of the series for $\psi(v)$, and we confine ourselves to the terms:

$$\phi(v) = -\alpha + 3\gamma v^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

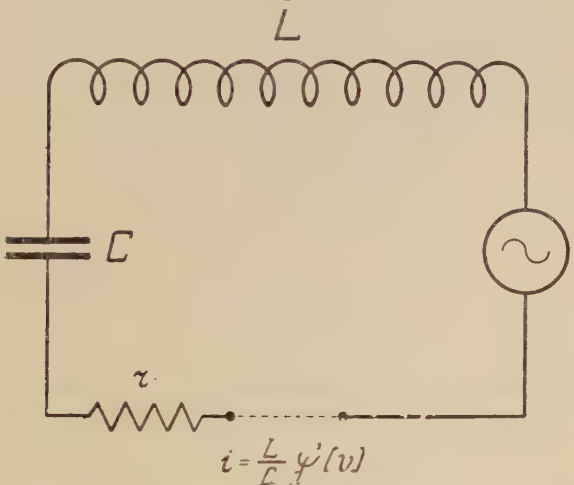
in which α and γ are positive quantities.

The fundamental differential equation now becomes

$$\ddot{v} - \alpha\dot{v} + \gamma\frac{dv^3}{dt} + \omega_0^2 v = B\omega_1^2 \sin \omega_1 t. \quad . \quad . \quad . \quad (1)$$

If the third non-linear term, $\gamma\frac{dv^3}{dt}$, were absent, formula (1) is reduced to the well-known differential equation for forced oscillations.

Fig. 1.



The new term γ, which follows logically from the characteristic curves, suddenly introduces all the peculiarities discussed in § 1.

§ 3. The case wherein the receiving circuit is tuned, or nearly so, to the received oscillations is of prime interest. Hence we try for the general solution of (1) the expression

$$v = b_1 \sin \omega_1 t + b_2 \cos \omega_1 t, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which b_1 and b_2 are functions of t but only slowly variable, viz. :

$$\dot{b}_1 << \omega_1 b_1,$$
$$\dot{b}_2 << \omega_1 b_2,$$

and

$$\ddot{b}_1 << \omega_1 \dot{b}_1,$$
$$\ddot{b}_2 << \omega_1 \dot{b}_2,$$

so that $\ddot{b}_1$ and $\ddot{b}_2$ may be neglected.

The solution allows for the possibility of the presence of free oscillations, by the assumption that both b's are functions of t. This will be explained more fully further on. In the term v^3 we only retain the fundamental frequency such that

$$v^3 = \tfrac{3}{4}(b_1^2+b_2^2)(b_1 \sin \omega_1 t + b_2 \cos \omega_1 t). \quad . \quad . \quad (4)$$

By substituting (3) and (4) in (1) and separately equating the terms containing $\sin \omega_1 t$ and $\cos \omega_1 t$ to zero, we have:

$$\left.\begin{aligned} 2\dot{b}_1 + z b_2 - \alpha b_1 \left(1 - \frac{b^2}{{a_0}^2}\right) &= 0, \\ 2\dot{b}_2 - z b_1 - \alpha b_2 \left(1 - \frac{b^2}{{a_0}^2}\right) &= \mathrm{B}\omega_1, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (5)$$

in which

$$\left.\begin{aligned} z &= \frac{{\omega_0}^2 - {\omega_1}^2}{\omega_1} \fallingdotseq 2(\omega_0 - \omega_1), \\ b^2 &= b_1^2 + b_2^2, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (6)$$

and

$$a_0^2 = \frac{\alpha}{\frac{3}{4}\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

represents the amplitude of the free stationary oscillation.

§ 4. Before completing the solution of the non-linear case, two particular cases will be investigated first. In the first case we will investigate whither the present mode of solution, which differs from those usually adopted, will lead us in a linear case. To this end we assume in (7) that

$$\gamma = 0,$$

so that a_0^2 becomes ∞.

This has the effect of simplifying (5) to

$$\left.\begin{aligned} 2\dot{b}_1 + z b_2 - \alpha b_1 &= 0, \\ 2\dot{b}_2 - z b_1 - \alpha b_2 &= \mathrm{B}\omega_1 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

the solutions of which are:

$$\left.\begin{aligned} b_1 &= e^{\frac{\alpha}{2}t}\left(\mathrm{C}_1 \sin \frac{z}{2}t + \mathrm{C}_2 \cos \frac{z}{2}t\right) - \frac{z\omega_1 \mathrm{B}}{z^2+\alpha^2}, \\ b_2 &= e^{\frac{\alpha}{2}t}\left(-\mathrm{C}_1 \cos \frac{z}{2}t + \mathrm{C}_2 \sin \frac{z}{2}t\right) - \frac{\alpha\omega_1 \mathrm{B}}{z^2+\alpha^2} \end{aligned}\right\}.$$

b_1 and b_2 are therefore of a slow periodicity. By substituting these in (3) we obtain the following equation for v :

$$v = C_3 e^{-\frac{\alpha}{2}t} \sin(\omega_0 t + \phi) + \frac{B\omega_1}{\sqrt{(\omega_0-\omega_1)^2+\alpha^2}} \sin\left(\omega_1 t + \tan^{-1}\frac{2\alpha}{\omega_0-\omega_1}\right),$$

which expression agrees with the exact linear solution of (1) if we neglect the frequency correction to which the free oscillations are subjected on account of the resistance. Hence the free oscillations are represented by the slow periodic part of the b's.

Secondly, we will consider the case in which the external E.M.F. B is equated to zero.

Expression (5) then leads to

$$b_1 = \frac{a_0 \cos\left(\frac{z}{2}t+\phi\right)}{\sqrt{1+Ce^{-\alpha t}}},$$

$$b_2 = \frac{a_0 \sin\left(\frac{z}{2}t+\phi\right)}{\sqrt{1+Ce^{-\alpha t}}};$$

so that in this case we obtain for the solution of the (only present) free oscillation in (1) :

$$v = \frac{a_0 \sin(\omega_0 t+\phi)}{\sqrt{1+Ce^{-\alpha t}}},$$

which agrees with our previous solution *.

§ 5. Returning again to the solution of the general problem, we find that a particular solution of (5) is given by

$$\dot{b}_1 = \dot{b}_2 = 0,$$

so that

$$\left.\begin{aligned} zb_2 - \alpha b_1\left(1-\frac{b^2}{{a_0}^2}\right) &= 0, \\ -zb_1 - \alpha b_2\left(1-\frac{b^2}{{a_0}^2}\right) &= B\omega_1; \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (8)$$

whence

$$z^2 + \alpha^2\left(1-\frac{b^2}{{a_0}^2}\right)^2 = \frac{B^2{\omega_1}^2}{b^2}. \quad . \quad . \quad . \quad . \quad (9)$$

* *Tijdschr. v. h. Ned. Radiogen.* i. p. 21 (1920).

In this instance we are dealing solely with the presence of forced oscillation, seeing that both b's in this particular solution are independent of the time. The free oscillations, which are represented by periodic parts of the b's, are here completely absent.

The circumstances under which this condition obtains are determined by a further stability investigation.

To effect this we will consider small variations Δb_1 and Δb_2 from the solutions b_1 and b_2 as obtained from (8), and determine whether or not these deviations approach 0 with the time.

From (5) and (8) follows a linear equation for both Δb's (with $\mathrm{D} = \frac{d}{dt}$):

$$\left[4\mathrm{D}^2 - 4\alpha\mathrm{D}\left(1-\frac{2b^2}{a_0^2}\right) + \alpha^2\left(1-\frac{b^2}{a_0^2}\right)\left(1-\frac{3b^2}{a_0^2}\right)+z^2\right]\begin{Bmatrix}\Delta b_1\\ \Delta b_2\end{Bmatrix} = 0. \qquad (10)$$

The solution (10), which has the form

$$x^2 + ex + f = 0,$$

only approaches zero with the time when

$$e > 0 \quad \text{and} \quad f > 0.$$

Hence the solution (8) is only stable when

$$b^2 > \tfrac{1}{2}a_0^2, \qquad (11)$$

and

$$\alpha^2\left(1-\frac{3b^2}{a_0^2}\right)\left(1-\frac{b^2}{a_0^2}\right)+z^2 > 0. \qquad (12)$$

The first, (11), of these conditions required for the stable solution of (8, 9), *i.e.*, where the free oscillations are suppressed by the forced oscillations, may be put in words as follows:—

The development of the free oscillation is suppressed if the square of the resultant amplitude of the forced oscillation is greater than half the square of the amplitude which the free oscillation would attain in the absence of an external E.M.F.

The second condition, (12), for the suppression of the free by the forced oscillation may also be written

$$\frac{db^2}{d\mathrm{B}^2} > 0 \qquad (12\,a)$$

or

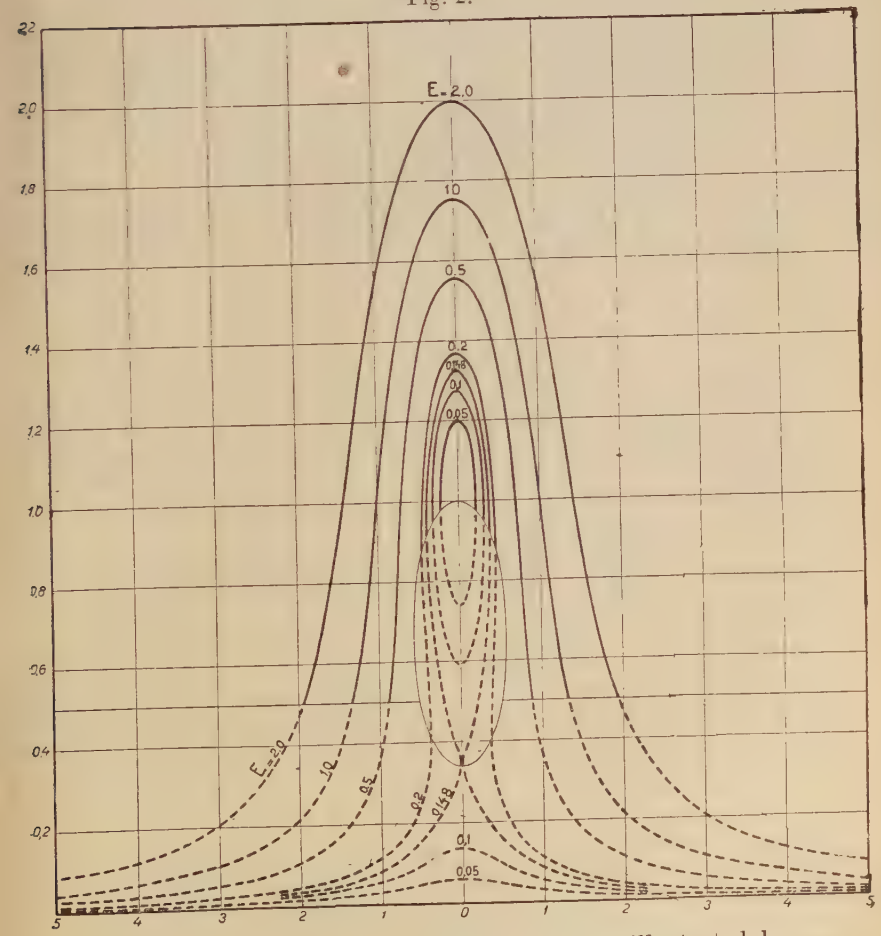
$$\frac{db^2}{dz^2} > 0; \qquad (12\,b)$$

i. e.:

Free oscillations are also suppressed by the forced oscillations if in (9) *of the three available values of* b^2 *of the forced oscillations, such a value is chosen that the amplitude increases with increasing external E.M.F. This is quite a plausible condition.*

Condition (12 *b*) simply lays down that *a stable solution is only obtained provided that an increased amplitude results from an increased accuracy in tuning.*

Fig. 2.



§ 6. The results obtained up to now are illustrated by a few resonance curves given in fig. 2.

To this end (9) may be written

$$x^2+(1-y)^2=\frac{\mathrm{E}}{y}, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

in which

$\frac{z}{\alpha}=x$ represents the amount of detuning,

$\frac{b^2}{{a_0}^2}=y$ „ the resultant amplitude,

$\frac{{\omega_1}^2\mathrm{B}}{a_0}=\mathrm{E}$ „ the external E.M.F.

The x used in fig. 2 thus measures the degree of detuning, and the ordinate y the resultant amplitude of the forced oscillation for the following values of the external E.M.F.:

$$\mathrm{E}=0{\cdot}05 \quad 0{\cdot}1 \quad 0{\cdot}148 \quad 0{\cdot}2 \quad 0{\cdot}5 \quad 1{\cdot}0 \text{ and } 2{\cdot}0.$$

Stable conditions are shown by full lines, whilst unstable conditions are represented by the broken lines. The unstable portions are according to (11) and (12) limited by the curves

$$y=\tfrac{1}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and

$$(1-3y)(1-y)+x^2=0, \quad . \quad . \quad . \quad . \quad (15)$$

which areas are bounded by thin lines in the figure.

Fig. 2 clearly shows that for a strong signal, in which case $\mathrm{E}=2$, the resultant amplitude attains a maximum when the circuit is in tune, dropping off to each side of the maximum in a manner practically similar to the ordinary (linear) resonance curve.

The slope of the resonance curve is, however, smaller than that obtained with a linear resistance for the same resonance amplitude.

The shape of the $\mathrm{E}=2$, $\mathrm{E}=1$, and $\mathrm{E}=0{\cdot}5$ curves is roughly similar; for weaker signals, *i. e.* when $\mathrm{E}=0{\cdot}2$ and $0{\cdot}148$, the resonance curves are slightly "waisted." They are, however, only stable up to the point where the slope becomes vertical, as for stability the condition

$$\frac{db^2}{dz^2}>0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12\,b)$$

must be satisfied.

When the signals are very weak, $\mathrm{E}=0{\cdot}1$ and $0{\cdot}05$, the resonance curve splits up into two parts, the upper part assuming an approximately elliptical form, the lower part rising to a slight maximum. This lower part, falling below

the value $y=\frac{1}{2}$, is unstable as shown by (11), and need not be further discussed ; the upper portion is elliptical and only stable up to the point where the curve becomes vertical.

§ 7. We still have to consider the disturbance occurring outside the limits of stability of $b^2=$const. Experiments go to show that the solution is now no longer of single periodicity, and thus may be regarded as the point at which free oscillations set in. Therefore, if an unmodulated carrier wave is being received, nothing will be heard in the region for which a stable solution of $b^2=$const. is obtained. As soon, however, as the boundary of the stability is crossed, the familiar heterodyne note will be heard.

Fig. 2 shows that the width of this "silent region" increases with the strength of the incoming signals E. For *weak signals* this width is given by

$$x^2+(1-y)^2=\frac{\mathrm{E}}{y} \quad . \quad . \quad . \quad . \quad (13)$$

and

$$x^2+(1-y)(1-3y)=0. \quad . \quad . \quad . \quad . \quad (15)$$

If the *signals* are *strong*, the width of the silent region is determined by

$$x^2+(1-y)^2=\frac{\mathrm{E}}{y} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and

$$y=\tfrac{1}{2}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The last expression may also be written

$$(\omega_0-\omega_1)^2+\tfrac{1}{16}\alpha^2=\frac{\omega_1{}^2\mathrm{B}}{2a_0{}^2}, \quad . \quad . \quad . \quad . \quad . \quad (m)$$

or, for very strong signals, where

$$\tfrac{1}{16}\alpha^2<<(\omega_0-\omega_1)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (n)$$

the expression becomes

$$\frac{\omega_0-\omega_1}{\omega_1}=\mp\frac{\mathrm{B}}{\sqrt{2}\,.\,a_0}. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Expression (16) is therefore only valid for very strong signals, and has for this case been confirmed experimentally by Dr. Appleton *.

* Appleton, Proc. Camb. Phil. Soc. *l. c.*

8. The disturbance beyond the limits of the silent region is given by (5), in which the b's are to be taken as functions of the time. We have not so far succeeded in obtaining a general solution for (5). It is possible, however, to determine the point at which free oscillations would set in on the borders of the silent region, by determining the small deviations Δb from b at that point. Thus for weak signals, for which (12) is valid, expression (10) gives us on the borders of the silent region :

$$\Delta b_1 = C_1 + C_2 e^{a\left(1-\frac{2b^2}{a_0^2}\right)t}.$$

The second term in this expression diminishes to zero with the time, and the equilibrium at that point is therefore indifferent.

For stronger signals, the stability conditions of which are determined by (11), we obtain in the same way from equation (10) the following expression for Δb_1 at the border :

$$\Delta b_1 = C_3 \sin\left(\frac{1}{2}\sqrt{z^2-\frac{\alpha^2}{4}}\,.\,t+\psi\right)$$
$$= C_3 \sin\left(\sqrt{(\omega_0-\omega_1)^2-\frac{\alpha^2}{16}}\,.\,t+\psi\right).$$

The free frequency with which the circuit commences to oscillate spontaneously at the border is not ω_0, but is expressed by

$$\omega_1-\sqrt{(\omega_0-\omega_1)^2-\frac{\alpha^2}{16}}. \quad . \quad . \quad . \quad . \quad (17)$$

Hence the free frequency undergoes a correction in the direction of the forced frequency, giving the impression as if the free frequency were being attracted by the forced frequency. This correction of the free frequency has experimentally already been noted by Vincent, Möller, and Appleton.

§ 9. As a first approximation of a particular solution of (1) at a point far outside the resonance region, it is permissible to assume a linear combination of the free and forced oscillations, viz. :

$$v = a \sin(\omega_0 t+s)+b \sin(\omega_1 t+\lambda), \quad . \quad . \quad (18)$$

in which a, b, s, and λ are constants.

If only the frequencies ω_0 and ω_1 are retained in v^3, we have

$$v^3 = \tfrac{3}{4}[a(a^2+2b^2)\sin(\omega_0 t+s)+b(b^2+2a^2)\sin(\omega_1 t+\lambda)]. \quad . \quad . \quad . \quad (19)$$

On substituting (18) and (19) in (1), equating the terms containing $\sin\omega_0 t$, $\cos\omega_0 t$, $\sin\omega_1 t$, and $\cos\omega_1 t$ to zero, and neglecting the small terms, we obtain the following four equations :

$$\left.\begin{aligned} \omega_0-\omega_0 &= 0, && (a)\\ a\left(1-\frac{a^2+2b^2}{a_0^2}\right) &= 0, && (b)\\ b\,\frac{z}{\omega_1} &= -\mathrm{B}\cos\lambda, && (c)\\ \frac{\alpha}{\omega}b\left(1-\frac{b^2+2a^2}{a_0^2}\right) &= -\mathrm{B}\sin\lambda. && (d) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (20)$$

Equation (20 *a*) shows that the choice of the free oscillation frequency in (18) without correction was right as a first approximation. The symbol s does not appear in (20), which indicates that we are free to make an arbitrary choice in regard to the phase. Expression (20 *b*) resolves into the following two solutions :

$$a = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$1-\frac{a^2+2b^2}{a_0^2} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

The first solution represents the suppression of the free by the forced oscillation. This is therefore the solution applying to the silent region which has already been fully discussed; for, if (*c*) and (*d*) are squared and added together, we obtain equation (9).

Solution (22), on the other hand, admits of a finite amplitude being given to the free oscillation.

By eliminating a^2 from (22), (20 *c*) and (20 *d*) we obtain

$$z^2+\alpha^2\left(1-\frac{3b^2}{a_0^2}\right)^2 = \frac{\mathrm{B}^2\omega_1^2}{b^2}. \quad . \quad . \quad . \quad . \quad (23)$$

If (23) be compared with (9) it will be seen that owing to the presence of the free oscillations the circuit behaves with regard to the forced oscillations as if γ, which indicates the change in resistance with the amplitude, had been multiplied by 3.

Equation (22) shows moreover that the free amplitude (a^2) cannot develop to a_0^2 but only to

$$a^2 = a_0^2 - 2b^2,$$

from which it follows that, as soon as the forced amplitude equals

$$b^2 = \tfrac{1}{2}a_0^2,$$

no room remains for the free oscillation, seeing that a^2 would become negative. As soon as this occurs the free oscillation is suppressed by the forced oscillation. This agrees with the results given by equation (11) indicating the same limiting value.

§ 10. The results obtained in § 9 enable us to extend fig. 2 to the curves given in fig. 3. The mean square of the total disturbance in the presence of free oscillations is given by

$$\tfrac{1}{2}(a^2+b^2).$$

The curves in fig. 3 are, within the silent region, the same as those shown in fig. 2 ; outside this region, where free oscillations are present, the quadratic amplitude a^2+b^2 has been plotted in accordance with equations (23) and (22).

Fig. 3 shows that a good connexion has been established between solutions (9) and (23), especially where the external E.M.F. is high. However, where

$$\mathrm{E} = \frac{\omega_1^2 \mathrm{B}^2}{a_0^2} = 0{\cdot}2 \text{ to } 0{\cdot}05$$

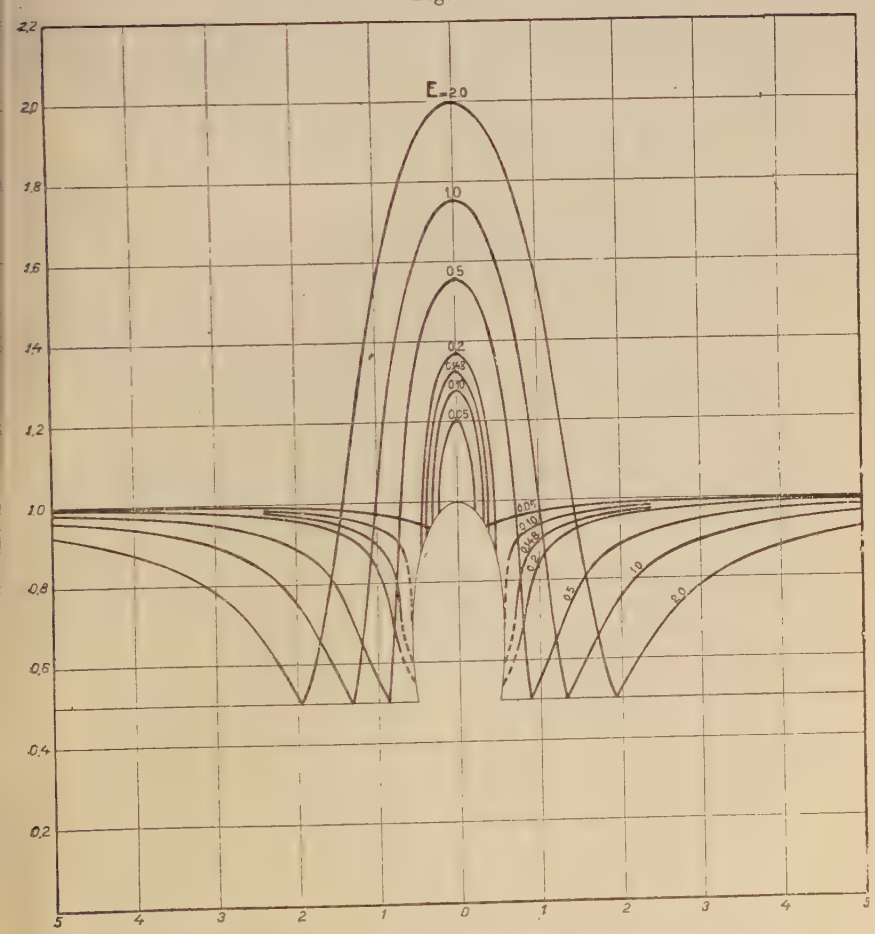
we encounter a small region, shown dotted in the figure, where the connexion is not complete. Only a complete solution of (5) could establish such a connexion. If fig. 3 be further compared with the experimental results obtained by Möller, it will be seen that these are in excellent agreement. (See also J. Golz, *Jahrb. Drahtl. Tel.* xix. p. 281, 1922.)

It may at first appear somewhat strange that the mean square of the disturbance, as shown in fig. 3, is sometimes smaller under the influence of an external E.M.F. than that obtained when free oscillations only are present.

In a physical way, however, this result may be roughly interpreted as follows :—If free oscillations only are present, the amplitude attained is determined by the curvature of the characteristic. If in addition a forced oscillation is present,

the representative point will tend to oscillate on such parts of the characteristic where the slope is smaller, resulting in a reduction of the mean negative resistance available for the free oscillations. This effect more than counterbalances

Fig. 3.



the contribution made by the free oscillations to the mean square total amplitude, the net result of which is that the latter decreases in consequence of the simultaneous presence of the two oscillations.

Summary.

If a triode system which is reaction-coupled beyond the critical point is acted upon by a signal in the form of a continuous wave, the circuit must satisfy the following equation (secondary factors being eliminated) :

$$\ddot{v}-(\alpha-3\gamma v^2)\dot{v}+\omega_0^2 v = B\omega_1^2 \sin \omega_1 t, \quad . \quad . \quad . \quad (1)$$

in which the non-linear term containing γ is essential in order to represent the experimental facts. In the absence of an external E.M.F., *i. e.* without the right-hand term, this equation gives us a free oscillation of frequency ω_0 having a constant amplitude a_0 determined by

$$a_0^2 = \frac{\alpha}{\frac{3}{4}\gamma}.$$

If an external E.M.F. is present, the following phenomena are observed :—

Close to the resonance region (ω_1 practically equal to ω_0) forced oscillations only are present the amplitude of which is greater than a_0. At this point the free oscillations are suppressed by the forced oscillations. Moving away from the resonance region, by varying ω_0 the amplitude of the forced oscillation decreases until it falls below a_0. Continuing this detuning, the free oscillations commence to set in with a small amplitude ; the latter are subjected, however, to a small frequency correction in the direction of the forced oscillation frequency. The mean square of the total disturbance, consisting of free and forced oscillations, is smaller than that set up by the free oscillations only.

The limits of stability of the suppression of the free oscillations are investigated in detail.

The total disturbance is generally regarded as an oscillation of forced frequency, the amplitude of which may be slowly variable.

If this amplitude is constant, the forced oscillation only is present. If in addition to the constant part of the amplitude, a slow and periodic variation of the amplitude is found, this would indicate simultaneous presence of free and forced oscillations. These oscillations react on one another due to the non-linear term containing γ in the equation, as opposed to cases of linear form in which this interaction is absent.

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VIII. *A Hot-Wire Instrument for measuring Speed and Direction of Airflow.* *By* L. F. G. Simmons, *M.A.*, *and* A. Bailey, *M.Sc.*, *of the National Physical Laboratory* *.

[Plate II.]

Abstract.

A form of hot-wire speed and direction meter suitable for use over a large range of wind speed, and possessing a high order of directional sensitivity, is described at some length. Its development is traced from the initial stages of a wire set along the wind to its ultimate form consisting of a grouping of three wires.

Measurements of airflow behind a finite aerofoil made with the three wire-instrument are included for purposes of comparison with corresponding measurements obtained with the standard form of tube instrument.

IT may be taken as axiomatic that the most satisfactory form of speed and direction meter for general use is one which responds readily to small changes in the flow, in such a manner that they can be followed with reasonable precision. This implies small inertia of moving parts with sufficient damping to make the instrument more or less dead-beat. In the tube form of meter these conditions are not fulfilled; by reason of the excessive damping the instrument is slow in action, and observations with it are rendered laborious and somewhat difficult to obtain. As there does not appear to exist any method by which the damping can be reduced without increasing the size of the tubes and thereby increasing the interference on the local flow, it is necessary to seek improvement along other lines.

The hot-wire anemometer offers a solution. Free from the disadvantages common to tubes, this type of instrument is noted for the rapidity with which it responds to an alteration of speed: also it can be made small so as to present little obstruction to the flow. In its common form, however, where the wire is placed normal to the stream for speed measurement, a large angular displacement from this position has no appreciable effect on the

* Communicated by E. F. Relf, A.R.C.Sc.

rate of cooling, and therefore the instrument requires to be modified before it can be used as a directional indicator.

A special form of hot-wire speed and direction meter has been previously described by one of the authors *. This form of instrument was shown to be suitable for speeds below about 20 ft./sec. ; and although a modification was tried with the object of extending its application to higher speeds, it met with only partial success.

Recently, as a result of experiments to be described later, a new form of hot-wire instrument has been constructed and used for measuring the speed and direction of airflow. Although primarily designed for the laboratory, it may, in a modified form, have a wider application. For this reason its development is here traced at some length from the initial stages of a single wire, set along the wind, to its present form consisting of a pyramidal grouping of three wires.

Heat-loss from Wires when placed at various Angles of Incidence in an Air Current.

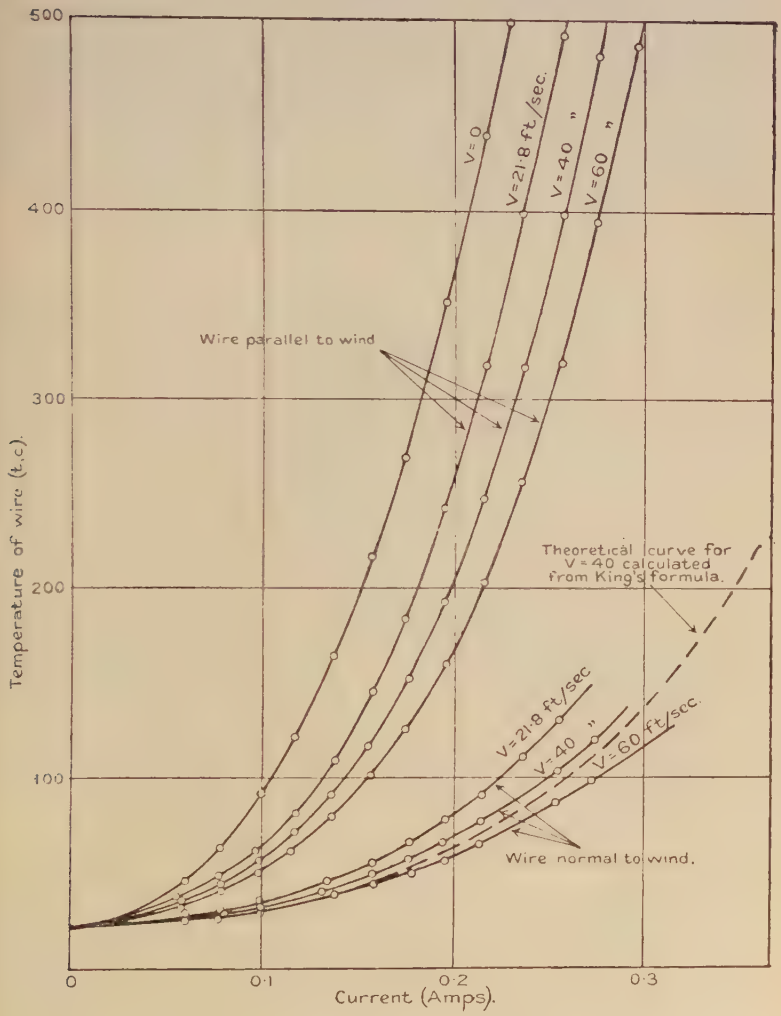
The first object of the experimental investigation was to determine whether, and if so under what conditions, a heated wire can be used to measure both speed and direction of airflow. A platinum wire of 0·00105 inch † diameter and 3·07 inches in length was selected for the experiments because of its high resistance-temperature coefficient, combined with its ability to withstand high temperatures without oxidization of the surface. The wire was heated by an electric current; and both resistance and current were measured by a potentiometer method, by comparing the potential difference between the ends of the wire with that across a standard resistance placed in series.

The results furnished by the preliminary experiments show definitely that the resistance, and hence the temperature, of a wire heated by a constant current depends upon the inclination of the wire to the wind direction.

* Aeronautical Research Committee, Reports and Memoranda, No. 777 : "A Directional Hot-wire Anemometer," by A. Bailey.

† The diameter of the wire was measured by an optical method in the Metrology Department of the Laboratory, and is probably correct to within $\pm$ 1 per cent. Other methods involving the use of micrometers were also tried, but it was found that the deformation due to the small contact pressure was sufficient to produce errors of about 10 per cent. in the measurement of the diameter.

Fig. 1.

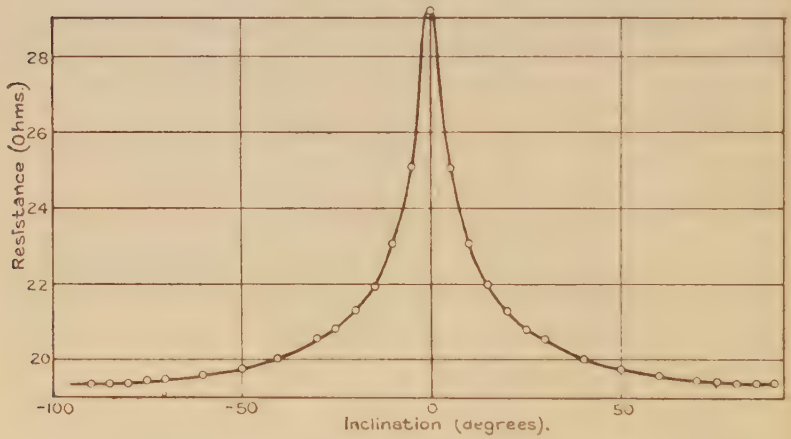


(*t*, *c*) curves for a platinum wire (length=3·07 ins., diam.=0·00105 in.) when set parallel and normal to the air current, at speeds of 21·8, 40, and 60 ft./sec.

Air temperature=22° C. approx.

Thus from fig. 2 it will be seen that the resistance reaches a maximum when the wire is parallel to the stream, and a minimum when the wire is in the normal position. About 50 per cent. of the difference between the maximum and minimum values, amounting generally to several ohms, occurs between the angular positions of 0° and 10° ; when it is remembered that resistance measurements can be made to a high degree of accuracy it will be readily appreciated that a heated wire, inclined at a small angle to the wind, possesses directional qualities of a high order.

Fig. 2.



Resistance of heated wire (diam.=0·00105 in., length =3·07 ins.) at various inclinations to the wind direction; current maintained constant =0·215 amp. Wind speed=40 ft./sec.
Each observation represents the mean of a large number of readings.

Fortunately it can also be satisfactorily employed, in this position, as an anemometer. This is best shown from a comparison of the rate of heat loss with the wire parallel to the direction of air movement at a number of wind speeds, with the corresponding losses when the wire is normal to the flow, the latter being taken as representative of conditions obtaining in current practice.

Reference should here be made to fig. 1, where temperature, deduced from resistance measurements, is plotted against current for a number of wind speeds. The results may

be expressed as follows :—

Wire normal to airflow :

$$H = 6{\cdot}68 \times 10^{-5} V^{\frac{1}{2}} + 9{\cdot}60 \times 10^{-5}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Wire parallel to airflow :

$$H = 1{\cdot}673 \times 10^{-6} V + (1{\cdot}0 \times 10^{-4} + 7{\cdot}5 \times 10^{-8} t). \quad . \quad (2)$$

Where $H = {\cdot}24C^2R$ = rate of heat loss in calories, per foot, per 1°C. difference of temperature,

V = wind speed ft./sec.,

t = temperature of wire in °C.

It is interesting to note that when allowance is made for the loss of heat to the supports (obtained from a comparison of the measured emissivity of the wire in still air with the figures given by Ayrton & Kilgour *) the corrected values of the rate of heat loss from a wire placed across the current are in excellent agreement with those calculated from King's formula, viz.,

$$H = 2\sqrt{\pi K s \sigma a}\, V^{\frac{1}{2}} + K,$$

where K = coefficient of conductivity of air, s = specific heat at constant volume, σ = density, a = radius of wire.

From equations 1 and 2 it is possible to estimate the sensitivity of the wire when used as an anemometer both parallel and normal to the stream. There are two conditions to be considered, according as to whether the constant current or the constant resistance method is adopted for the determination of speed : in the one case, the sensitivity is expressed as a percentage change in R, in the other, as a percentage change in C, due to a 1 per cent. change in V. Figures are given in the accompanying Table based on the results of fig. 1 which relate to a particular case of a wire heated to about 500° C, and used at a wind speed of 40 ft./sec. An examination of these shows that, irrespective of the method employed for measuring the cooling, a wire can be used parallel, instead of normal, to the stream with a loss of sensitivity of only 20 per cent. Further, it will be seen that the constant current method leads to a uniform increase in sensitivity of 30 per cent. ; but this advantage is outweighed in practice

* Phil. Trans. Roy. Soc. vol. 183 (1892).

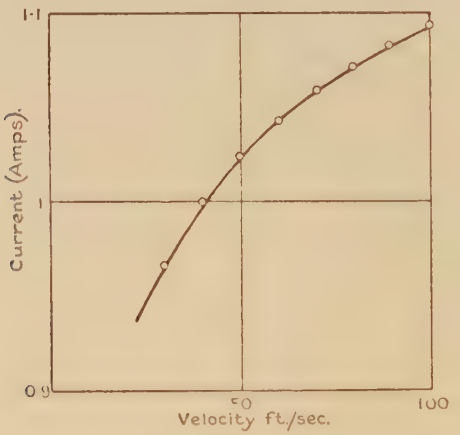
by the difficulties involved in keeping the current sufficiently constant, and actually the less sensitive method is preferred.

Changes in C and R due to a change of 1 per cent. in V.

Inclination of wire	Percentage increase in C (R constant).	Percentage increase in R (C constant).
0°	0·160	−0·211
90°	0·203	−0·264

As a practical method, the use of a single wire is subject to distinct limitations imposed by the irregular variations in direction and speed of airflow. Each type of disturbance independently affects the rate of cooling, and makes the process of setting the wire along the stream a matter of some difficulty, since this has to be effected by trial and error until the resistance is a maximum.

Fig. 3.

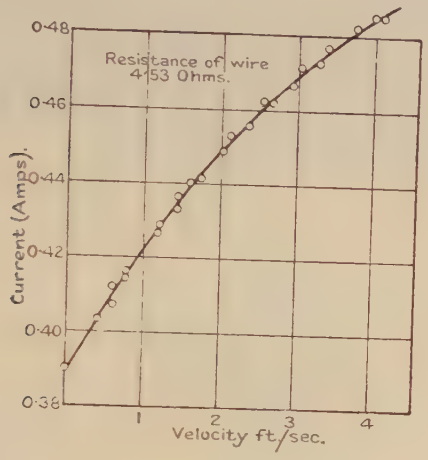


Calibration of short wire instrument (length 0·25 in.) set parallel to wind.

The degree of accuracy obtainable is consequently not high, as is confirmed by measurements which show that direction can be measured to within $\pm 0{\cdot}25°$ and speed to within 3 ft./sec. Where accuracy is not of first importance, the method can be conveniently employed for speeds up to, and greater than, 100 ft./sec., but for speeds below 5 ft./sec. the wire should preferably be supported in the normal position.

Typical calibration curves showing the relationship between C and V for two cases are given in figs. 3 and 4.

Fig. 4.



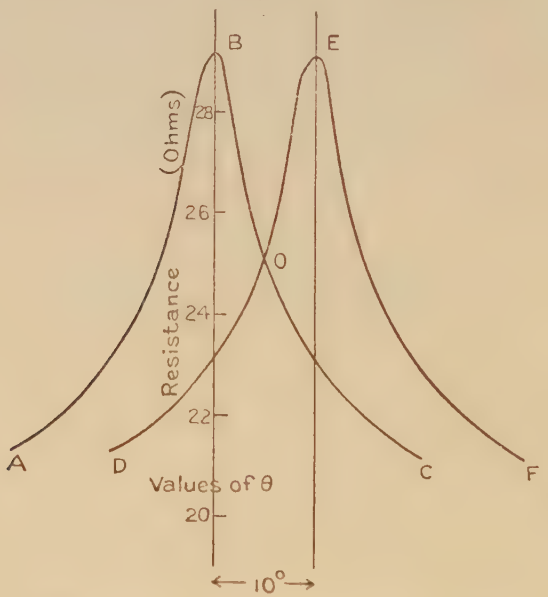
Calibration of short wire instrument (length 0·25 in.) set normal to wind, and used for measuring low speeds.

The Two Wire Instrument.

The effects of irregularities in the flow can be considerably minimized by the use of two similar wires instead of one. These are arranged in the opposite arms of a Wheatstone bridge, in which position the change of resistance of one wire due to a temporary disturbance is to a great extent counteracted by the corresponding change in resistance of the other. Moreover, the arrangement is more sensitive than the single wire, and provides a null method of measuring direction. This will be evident on reference to figs. 5 and 6, where ABC, DEF are the (R, θ) curves for the individual wires, displaced through 10°, and QRPS is the resultant found by subtracting the ordinates of the separate curves. From considerations of the slope of the resultant curve at the origin, it is clear that the combination is considerably more sensitive than a single wire ; and experiment shows that, due to this increased sensitivity coupled with the fact that the influence of irregularities in the flow on the rate of cooling is largely counteracted, it is easy to determine direction to an accuracy of 0°·05 in the plane of the wires.

For practical purposes the wires are conveniently soldered to thin manganin supports so as to form a small acute angle (see fig. 8). This angle should preferably be smaller than 10°, when experiment shows that the sensitivity is almost independent of wind speed: this is indicated in fig. 9, which shows graphically the difference of resistance of a wire when set along the wind and when inclined at a number of angles, at various wind speeds.

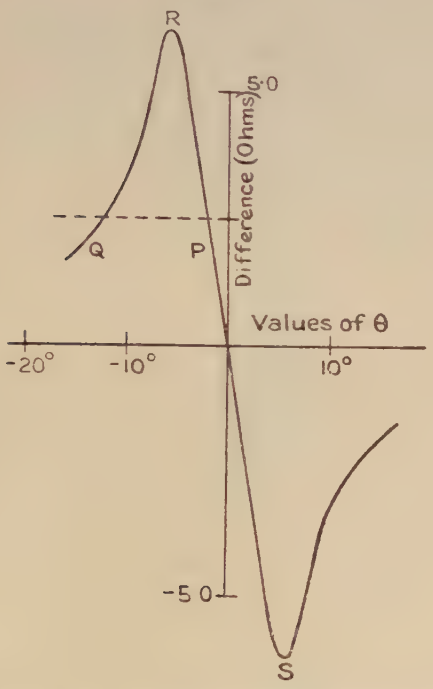
Fig. 5.



Effect of two wires inclined at 10° to each other.

The zero position of the instrument is such that the bisector of the angle formed by the wires lies along the wind; and, in order that this position shall be uniquely defined, it is necessary to effect a balance of the bridge at the mid-point between R and S (see fig. 6); otherwise there will always be two positions P and Q at which a balance will be possible, with no means of distinguishing between them. In practice this is conveniently secured by observing the deflexion of the galvanometer as the anemometer is rotated in a wind and noting the angular positions of R and S; afterwards, with the anemometer in the mean position, a small resistance r is introduced

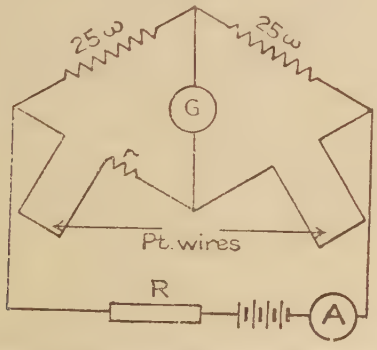
Fig. 6.



Effect of two wires inclined at 10° to each other

into the electrical circuit (fig. 7) to compensate for any dissimilarity between the two wires.

Fig. 7.

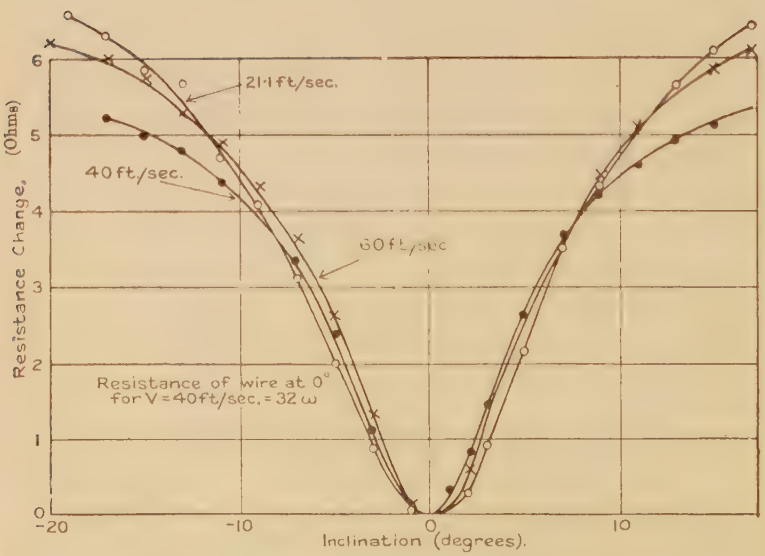


Arrangement of Wheatstone bridge for measuring direction with a two-wire instrument.

Fig. 8.

Two-Wire Direction Meter.

Fig. 9.



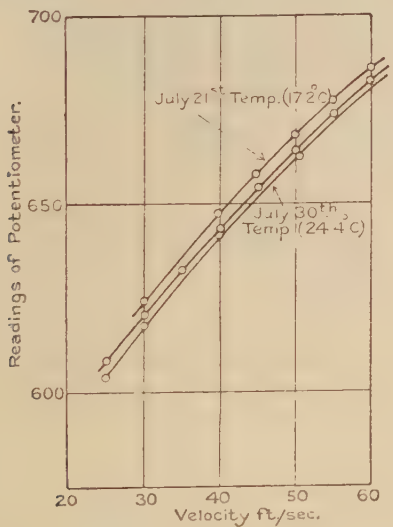
Effect of inclining wire at different wind speeds; current through wire maintained constant.

Measurements of speed are straightforward and require only brief mention. The method is substantially the same as that previously described, except that the two wires are now placed in series and balanced against a standard resistance, the position of the wires being, of course, that which gave a balance in the directional test. It should be observed, in passing, that a small displacement from this position has no appreciable effect on the speed indications, since the slope of the calibration curve at this point is zero. As before the constant resistance method is used, and the magnitude of the current to maintain a balance gives a measure of the speed.

The Three-Wire Instrument.

For exploring three-dimensional flow the two-wire instrument suffers in some measure from the disadvantage

Fig. 10.



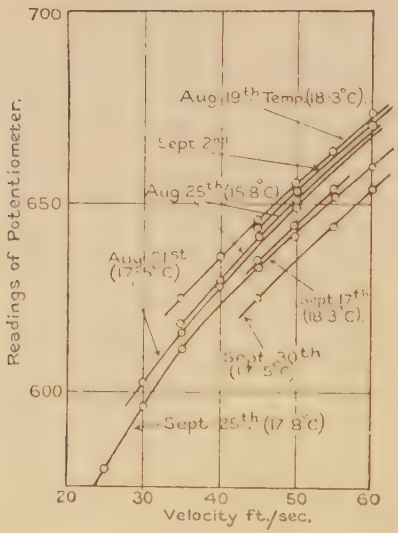
Calibrations of three-wire instruments. Air temperature given in brackets.

common to the single wire, inasmuch as it requires to be set with the wires in the plane of the wind ; this can only be done by determining the position of maximum resistance. To enable the setting to be accomplished with

greater ease and precision, an additional pair of wires may be added. The instrument then consists of four wires arranged so as to form the edges of a square pyramid, having a vertex angle of 10°. Each pair of opposite wires constitutes a separate exploring element (one pair in a vertical, the other in a horizontal plane), and these can be used independently for determining the horizontal and vertical components of velocity. A simplification can be introduced by making one wire common to each element, thus using three instead of four wires.

In the three-wire instrument as shown in fig. 17 *a* (Pl. II.)

Fig. 11.



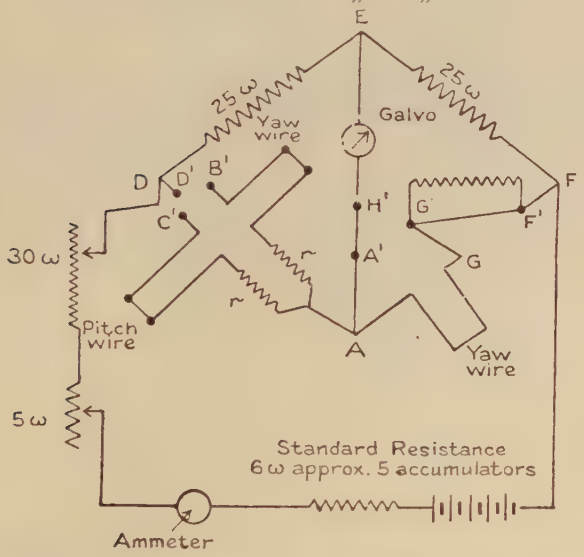
Calibrations of three-wire instruments. Air temperature given in brackets.

the wires are grouped symmetrically about an axis to form a regular pyramid of small vertex angle. When in use the axis of the pyramid is set along the direction of the local flow. To effect this the two lower, or "yaw," wires are used for rotating the instrument into the correct position about a vertical axis, whilst the third, or "pitch," wire, taken in conjunction with one of the other pair, is used for determining the correct attitude in pitch. Diagrammatic sketches of the electrical circuit employed for the measurements of direction are shown in fig. 12. The

fixed ratio arms of the bridge consist of manganin resistances of 25 ohms, whilst the third arm contains one of the platinum wires. Either of the remaining wires can be inserted at will into the fourth arm by means of a two-way switch.

Except that two compensating resistances are now required, one in series with each of the wires, the procedure followed in balancing the bridge initially is identical with that already described. With the bridge so adjusted,

Fig. 12.—Yaw and Pitch.
For Yaw D′ connected to B′.
For Pitch D′ „ „ C′.

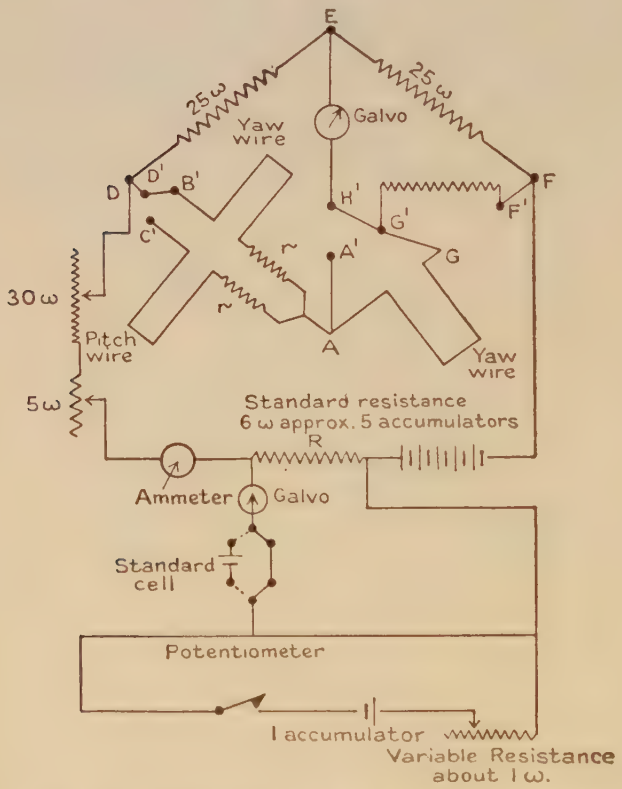


direction is determined by rotating the instrument first about a vertical axis, and afterwards about a horizontal axis, until a balance is obtained; the external current being maintained constant for the purpose at about 0·25 amp.

Speed is measured with the instrument at this attitude by connecting the yaw wires in series to form the third arm and balancing these against a constant standard resistance, inserted in the fourth arm of the bridge. As already mentioned, the resistance of the platinum wires depends upon the speed, so that the method virtually consists of measuring the external circuit necessary to preserve a balance. A direct measurement of the drop of potential across a standard resistance in the external circuit,

by the aid of a potentiometer (see fig. 13), provides a ready and accurate method for the purpose. Experience shows that an accuracy of 1 part in 5000 in the determination of the current is sufficient for most purposes.

Fig. 13.—Speed.



During the investigation of the flow in the wake of a finite aerofoil * measurements of speed and direction were made by means of the three-wire instrument and also with a standard tube instrument †. Figs. 14, 15, and 16 show graphically the three components of velocity U, V, and W deduced from the measurements at three sections: it will be seen that the agreement between the two sets of results is extremely satisfactory even under these exacting conditions, the only disagreement occurs in the values

* Fage and Simmons, Phil. Trans. Roy. Soc. vol. 225 (1925).

† T. Lavender, Aeronautical Research Committee Reports and Memoranda, No. 844.

Figs. 14, 15, and 16.

Comparison of observations taken with Hot-Wire and Tube Meters in the downwash behind an aerofoil.

All dimensions given in terms of chord length. Section two chords behind aerofoil.

	U	V	W
Hot-wire	+	•	×
Tube	⊙	○	⊕

Fig. 14.

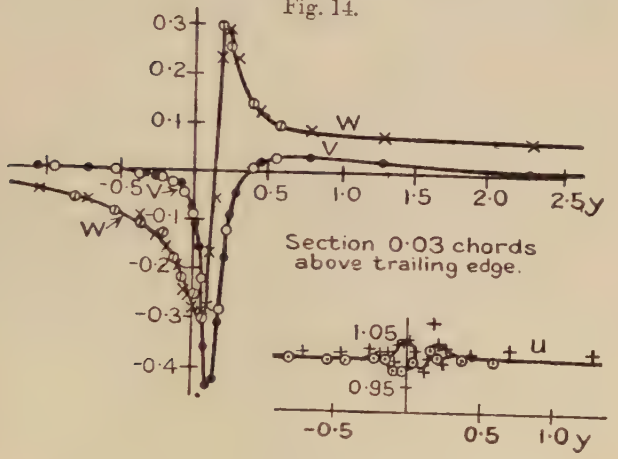


Fig. 15.

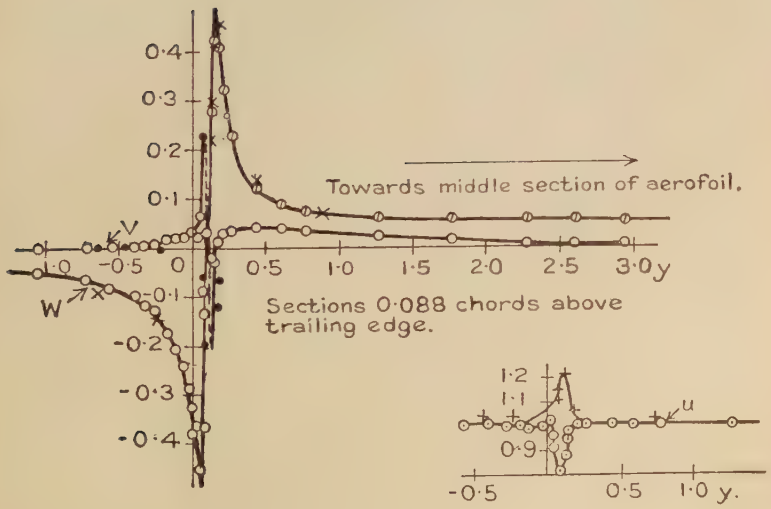
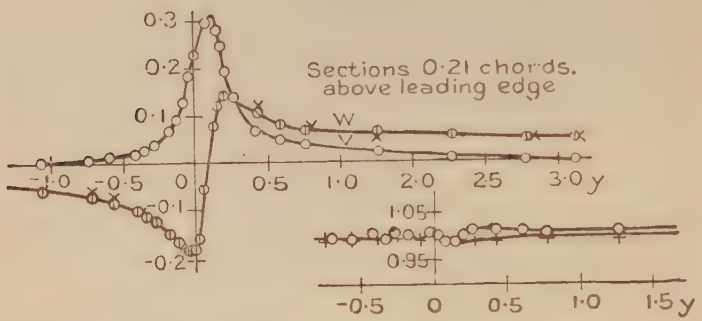


Fig. 16.



of U at the centre of an intense vortex region, where even the readings of the standard instrument may be open to doubt.

In the course of the investigation referred to above a fairly complete daily record of the calibration of the three-wire instrument was obtained over a period covering several days. Figs. 10 and 11 illustrate typical results for two instruments—in one case extending over a range of nine days, in the other, over six weeks. Both sets afford evidence of considerable and progressive variations with time, which cannot be ascribed to changes in the conditions of the surrounding air. This want of definiteness in the calibration, even although the wires are first annealed by slow cooling, from a high temperature, is the common defect of instruments of the hot-wire type; King * in particular refers to an "ageing" effect due to evaporation from the surface, and states that changes in the calibration may be greatly reduced by using the wire at a relatively low temperature. Contamination of the surface by dust particles has also been suggested as a possible cause, but this view does not receive support from experiments recently conducted by Zobel and Carroll †, who showed that the heat dissipated was not appreciably changed when the wire was thinly coated with dust or black shellac. All writers agree that strain, due to the aerodynamic forces, materially alters the diameter and length of the wire, and is an important factor in the problem. Until further information on the subject is available, it is therefore necessary to have recourse to frequent calibration. Even when allowance is made for daily calibration, however, the use of this instrument leads to a considerable saving of time as compared with the pressure type of direction and speed meter, except in cases where only a few readings are required.

* Phil. Trans. Roy. Soc. vol. 214 (1914).

† Paper No. 287, Bureau of Standards.

IX. *The Effect of Water on the Infra-Red Emission from the Flame and Explosion of Carbon Monoxide and Oxygen.* *By* W. E. Garner, *D.Sc., and* C. H. Johnson, *B.Sc.* (*Chemical Department, University College, London.*)

THE discovery by Dixon (Brit. Assoc. Report, 1880, p. 503) that carefully dried mixtures of carbon monoxide and oxygen could not be exploded by an electric spark led him to conclude that the formation of steam was an essential step in the reaction between these two substances ; thus :—

$$(1) \quad CO + H_2O \rightarrow CO_2 + H_2,$$
$$(2) \quad 2H_2 + O_2 \rightarrow 2H_2O.$$

The necessity for the presence of water is limited, however, to the initial stages of the process of combustion. This is clear from the experiments of Dixon, who has shown that in the explosion of dry cyanogen and oxygen the carbon monoxide produced behind the wave is completely burnt. Further, no effect on the speed of explosion of this mixture is observed on the addition of water. The freshly formed molecules of carbon monoxide can react readily with oxygen under the conditions ruling at the high temperatures of the explosion. Recently, Bone and Weston (Proc. Roy. Soc., A, vol. cx. p. 615, 1926) have established the correctness of this view by showing that carbon monoxide dried carefully over P_2O_5 for several months will explode with dry oxygen provided a sufficiently powerful spark be employed. Thus water acts as a catalyst for the reaction which proceeds readily enough at the high temperatures of the explosion.

A study of the infra-red emission spectra of flames and explosions of carbon monoxide and oxygen both in the dry and moist condition has thrown new light on the part played by water in accelerating the reaction. It has been shown that the intensity of the infra-red emission from the explosion of the dried gases is much greater than that from the moist gases (fig. 2). The effect is not due to increased absorption by the cold gases in front of the explosion wave, and it is very unlikely that it can be explained by an increase in the extinction coefficient of the hot gases in the wave itself due to the addition of water. The high transparency of the bunsen flame to its own radiation (Callendar, Brit. Assoc. Reports, 1910) is not in agreement with the view that water molecules are highly opaque at explosion temperatures.

* Communicated by the Authors.

The infra-red emission spectra from flames depends on the products of combustion and not on the substances burnt, as was shown by Julius and by the quantitative experiments of von Helmholtz. The spectrum emitted by carbon monoxide burning in oxygen corresponds very closely with the absorption and emission spectrum of carbon dioxide (Paschen, *Ann. Phys. Chem.* vol. lii. p. 214, 1894; Coblentz, Investigations of Infra-Red Spectra, Carnegie Publications, vol. xxxv., 1905). The agreement between these spectra is so close that there is a general consensus of opinion that the vibrating system responsible for the flame spectrum is the carbon dioxide molecule.

There has been much discussion as to the source of the infra-red emission from flames, whether this is entirely due to thermal emission from the hot gaseous products of the reaction as was maintained by Paschen, or whether an appreciable part of the chemical energy is liberated directly as radiation as was upheld by Julius, von Helmholtz, Pringsheim, and Smithells. With regard to infra-red radiation, most of the experimental evidence quoted as bearing on this point is of doubtful value on account of the difficulty of distinguishing between effects due to chemiluminescence and others caused by the departure from black-body conditions in the flame. The fact discovered by R. von Helmholtz ('Die Licht und Wärmestrahlung verbrennende Gase,' Berlin, 1890), that the infra-red emission from a flame is diminished by a preliminary heating of the gas and air, is free however from this objection. This experiment has recently been confirmed by Haslam, Lovell, and Hunneman (Ind. and Eng. Chem. xvii. p. 272, 1925). The decreased emission is explained by Helmholtz as caused by an increase in the rate of attainment of thermal equilibrium at the higher temperatures of the flame. In other words, the emission of chemiluminescence is decreased on preheating the gases on account of more rapid degradation of the chemical energy into thermal energy. Observations by David (Phil. Mag. xxxix. p. 66, 1920) support the view of Helmholtz that chemiluminescence is present in the infra-red radiation from flame. He finds that the rate of emission of radiation from explosions of coal and gas and air is greatest some time before the attainment of the maximum temperature of explosion. The maximum speed of emission of radiation appears to have been reached at the moment when the flame fills the explosion vessel, *i. e.*, when the chemical change is most rapid.

The evidence from our experiments on explosions of

carbon monoxide and oxygen points in the same direction. The augmentation of the infra-red emission which occurs on drying is accompanied by a decrease in the temperature of explosion : this result can be interpreted satisfactorily only if a portion of the radiation be chemiluminescence.

There is little doubt, however, both from the measurements of Paschen on the emission of hot gases, and of David on the emission from gaseous explosions, that part of the radiation has a thermal origin. Chemiluminescence, if it occurs, must be accompanied by thermal emission.

The above considerations lead us to put forward the view that the reduction in the intensity of the infra-red radiation, brought about by the addition of water, is due to collisions of water molecules with the freshly formed molecules of carbon dioxide, *i. e.* with the emitters of the 2·8 and 4·4 μ radiation. These molecules of carbon dioxide, in the absence of water, give up their excess of internal energy as infra-red radiation, but, when water is present, lose this energy by collision. The chemical and physical processes which occur can be represented by the following equation :—

$$2CO + O_2 \overset{1}{\rightleftharpoons} \left[\begin{array}{c} 2CO_2 \\ + \text{internal} \\ \text{energy} \end{array}\right] \overset{2}{\rightleftharpoons} 2CO_2 + \text{radiation}$$

$$+ \qquad\qquad + \qquad\qquad + \qquad\qquad +$$

$$X \qquad\qquad Y \qquad\qquad Z$$

$$\overset{4}{\swarrow} \qquad\qquad \overset{3}{\searrow} \qquad\qquad \overset{5}{\swarrow}$$

$$2CO_2 + \text{radiation} \qquad\qquad 2CO_2 + \text{thermal energy.} \qquad\qquad 2CO + O_2$$

The radiation emitted in the spontaneous change (2) lies in the infra-red at 2·8 and 4·4 μ. The collision of any molecule with an activated molecule of CO_2 may produce such a disturbance within the molecule that one of three events may occur : (*a*) it may drive back the reaction to $2CO + O_2$, this we are not concerned with at the moment ; (*b*) it may cause the emission of an infra-red quantum, or (*c*) it may degrade the internal energy into thermal energy. All of these processes may occur simultaneously in the gas mixture.

It is not possible to decide with any certainty whether the function of the water molecules is that of transforming the internal energy of the activated molecules of carbon dioxide into kinetic energy directly, or whether they act as carriers of energy to molecules of carbon monoxide. According to either of these mechanisms, some of the internal

energy of the freshly formed carbon dioxide which is normally emitted as radiation is retained in the gaseous mixture, and its retention serves to increase the rate of rise of temperature in the system. Thus the action of water and other positive catalysts which reduce the emission, *e.g.* ethyl iodide and ethyl nitrate, may be represented by (3) above. This does not rule out the possibility that the ordinary catalytic effects may be present also.

Substances which increase the intensity of infra-red emission, *e.g.* carbon tetrachloride and nitrogen peroxide, will diminish the rate of rise of temperature and exert a negative catalytic effect on the speed of explosion. The action of these substances can be represented tentatively by equation (4). The possibility should not be overlooked that they may produce the retardation of the velocity of explosion by removing traces of water present in the dried gases.

The acceleration or retardation of the velocity of explosion on the addition of the catalysts mentioned above is due in part at least to a change in the rate at which chemical energy is converted into thermal energy. The magnitude of the acceleration due to this cause can only be known when quantitative measurements of the intensities of emission have been made. Since the action of these catalysts presents features different from those of ordinary catalysis, it is proposed to describe them as *energo-thermic*, *i.e.* thermal energy catalysts.

Explosion Spectrum of a 2 : 1 *Mixture of Carbon Monoxide and Oxygen.*

The infra-red radiation from gaseous explosions has been the subject of many investigations by W. T. David during the last fifteen years. In his method of analysis, he determines the distribution of energy between the 2·8 and 4·4 μ bands, by measuring the intensity of the radiation which passes through windows of quartz and fluorite. This method of examination of the infra-red spectra from gaseous explosions is sufficient for many practical purposes. Since, however, it is important to study such problems as the broadening of the bands on increase in temperature and pressure, and the part played by the absorption of the cold gases in front of the explosion wave, it was felt that the determination of the complete infra-red spectrum by means of a rock-salt spectrometer would serve a useful purpose.

In the present paper an account is given of the experimental work on explosions of carbon monoxide and oxygen.

Apparatus.—The bomb in which the explosions were carried out was a centrally bored cylinder of phosphor-bronze about 40 cm. long and 2·5 cm. diameter. This was closed at one end by a phosphor-bronze plug carrying a fluorite window 1·7 cm. in diameter and 1 cm. thick. The effective diameter of the window was about 0·5 cm. The window was perfectly clear and its transparency to infra-red radiation was established before making up the bomb. The gas was introduced by means of a valve from the other end of the bomb. The length of the cylindrical space was 35 cm.

In order to secure rigidity during firing the bomb was clamped to a steel framework which kept its position fixed in relation to the spectrometer.

The spectrometer was of the Hilger pattern with the Wadsworth constant deviation device ; the rock-salt prism (60°) had a refracting edge of 7 cm. The thermopile supplied with the instrument, of the Rubens-Coblentz type, had twenty junctions and a resistance of about 12 ohms. It was particularly sensitive compared with others of the same type. The thermopile was protected from draughts and stray radiation by enclosing the arm carrying it in a brass case made to fit the instrument; as an extra precaution cotton-wool was wound round the case. The whole spectrometer was enclosed in a wooden box blackened on the inside, and the calibrated drum was observed with the aid of a telescope through a window in the side of the box and could be rotated by means of spools and thread from the outside. Thus radiation of any desired wave-length could be brought upon the thermopile without opening the box.

Two galvanometers have been used at different stages of the work ; both were of the Downing type. The first was kindly lent to us by Prof. A. V. Hill and was used in mapping the spectrum. With a full period of 2½ seconds, it had a sensitivity of 10^{-10}. The second galvanometer used later, purchased with the aid of a Brunner Mond grant, had a sensitivity of 10^{-12} with a period of about 6 seconds. Its suspension, consisting of a quartz fibre, 12 magnets and a mirror, weighed 3 to 4 mgm. (*cf.* Downing, J. Sci. Instruments, 1926). The galvanometer stood on a brick column built into the concrete foundations of the building, and mechanical vibrations were damped out by means of a pile of thick brown paper. No trouble was experienced from this cause. The galvanometer shield was constructed of μ-metal supplied by the Telephone Construction Co. and was found to be a considerable improvement upon the heavy

iron shields supplied with the Paschen galvanometer. The galvanometer and thermopile were connected through a pure copper two-way switch; to the other terminals of the switch was connected a circuit for supplying a constant small current to the galvanometer. The switch was enclosed in a box in order to protect it from draughts. The sensitivity of the galvanometer could thus be checked when required.

Explosion of Mixture saturated with Water Vapour.—The carbon monoxide was prepared from pure sodium formate and concentrated sulphuric acid and the oxygen prepared by heating pure potassium permanganate. Both gases were washed with strong potash solution, and after collecting in a gas holder stored in a reservoir over water. A mixture of carbon monoxide and oxygen in equivalent proportions was used throughout. Two or three days were allowed for the gases to mix thoroughly. The bomb was always filled to a pressure of 75 cm. and fired by fusion of 0·4 cm. of thin iron wire. After explosion the bomb was evacuated to 0·01 mm. for a definite period of time. When required, P_2O_5 tubes were inserted between the gas-holder and the bomb in order to dry the gas.

Experimental procedure.—The spectrometer was always set on the 4·4 μ maximum of the Meker burner prior to any experimental work, since this gave the same setting as the D sodium line. Once set correctly it was seldom that any change occurred during the course of a few hours. The sensitivity of the galvanometer was noted frequently, and only at very high sensitivities was any drift observed; under these conditions the sensitivity was measured after each reading.

The galvanometer deflexion during an explosion was noted by visual observation, and after a little practice this could be done quite accurately. Generally, conditions were steady enough to permit of work during the daytime; best results were obtained between 7 and 11 p.m., while occasionally work was done still later.

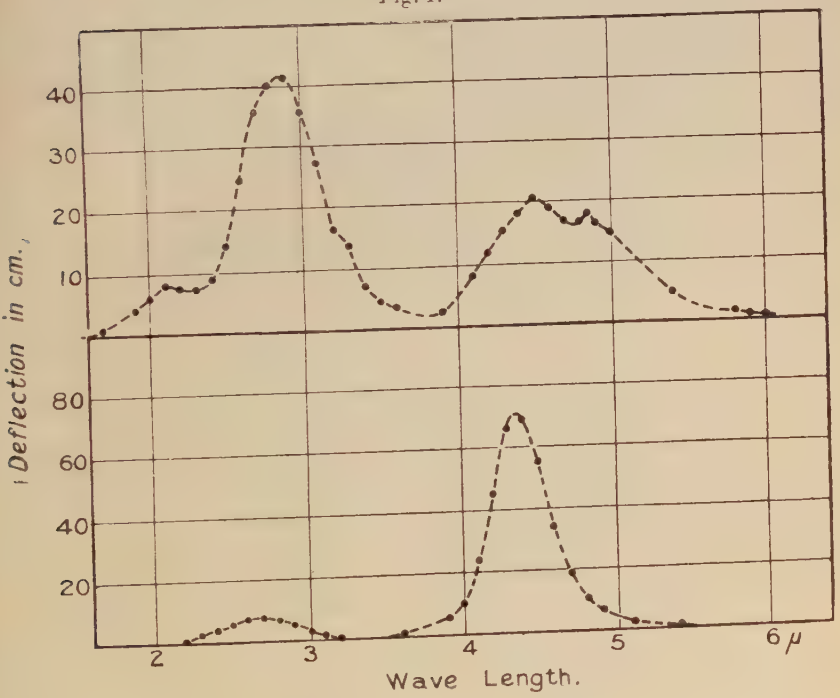
The spectrometer slit widths employed were 0·025 cm.

Experimental Results.—After a preliminary series of observations in the region 4·2 μ to 5·3 μ, which showed that the 4·4 μ band gave two maxima and was very broad, the results given in fig. 1 were obtained. Thirty-seven points are recorded for settings of the spectrometer between 1·3 and 6·1 μ; several of these were repeated and found to

check excellently. The explosion spectrum is compared with the infra-red spectrum of the flame of carbon monoxide and oxygen saturated with water vapour.

Examination of the explosion spectrum shows that with respect to the flame spectrum, both maxima are shifted slightly towards the longer wave-lengths. This is in agreement with the work of Paschen, who found that the maximum at 4·4 μ shifts towards the longer wave-lengths,

Fig. 1.



with increased temperature. Both bands appear to have broadened, the 4·4 μ band mainly on the side of the longer wave-lengths and the 2·8 μ band on the short wave-length side. Relatively more energy is registered in the 2·8 μ region for the explosion than for the flame. The ratio of the intensities of the two maxima 2·8 μ : 4·4 μ is about 2·3 : 1 for the explosion and 1 : 10 for the flame. This difference is partly due to absorption by carbon monoxide in front of the explosion wave; the two absorption regions of carbon monoxide at 2·3 μ and 4·6 μ are clearly seen upon the curve.

On making correction for this absorption the ratio for the explosion, viz. 1·3 : 1, is still widely different from that of the flame. The ratio of intensities of the radiation at 2·8 and 4·4 μ from a black body at 2500° C., *i. e.* the approximate temperature of the explosion, is 4 : 1. The experimental values of this ratio for the explosion and the flame are much lower. To what extent this is due to the departure from black body conditions is uncertain. It is not possible to conclude from these results alone that chemiluminescence is present in the radiation, for it has been calculated that the difference between the ratio for the flame and the black body, and between that of the explosion and the black body, could be entirely accounted for, were the ratio of the extinction coefficients of the two bands (2·8 : 4·4 μ) as low as 1 : 15 for the flame and 1 : 6 for the explosion. According to Coblentz (*loc. cit.*) this ratio is about 1 : 3 at 23° C.

Nevertheless in order to interpret the effect upon the infra-red emission of drying the explosive mixture, it seems necessary to adopt the view that some part of this difference is due to chemiluminescence.

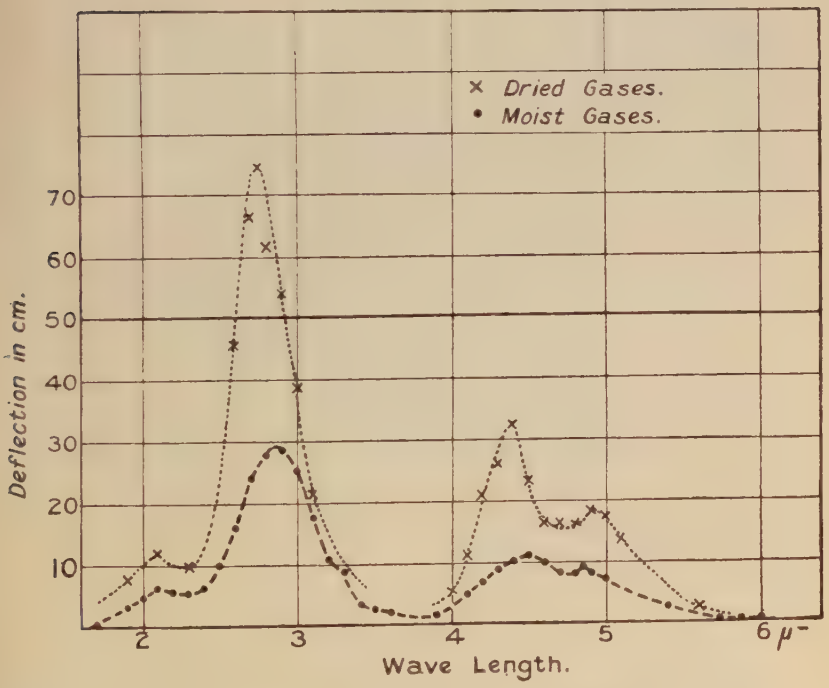
The Explosion of the Dried Gas Mixture.

The experiments can be conveniently discussed under two heads. First, the investigation of the effect of removal of water vapour upon the radiation at various points in the spectrum, and in particular at the two maxima. Second, the mapping of the complete dried gas spectrum.

Four series, comprising many readings, were carried out with different preparations of gas mixture. In one series, a small infra-red spectrometer and a somewhat less sensitive thermopile was used. The results were consistent and led to the following general conclusions. The removal of the greater part of the water vapour caused the deflexions (*i. e.* the energy emission) to increase generally throughout the spectrum. At all points off the 4·4 μ maximum there was an increase of about 60 per cent. in the emission. On the 4·4 μ maximum the increase was still more prominent; the deflexions obtained were three or four times as large as with the wet mixture. Moreover, the sensitiveness to small changes in water-content appeared to be very great in this region, and removal of the last traces of water brought about marked increase in the deflexions. The results are summarized in the following table.

μ.	Mean Deflexion Moist Gases.	Mean Deflexion Dried Gases.	Per cent. Difference.
2·4	8·5 cm.	13·5 cm.	60 per cent.
2·8	37·5 „	61·0 „	65 „ „
3·0	25·0 „	39·0 „	55 „ „
4·1	8·0 „	13·5 „	65 „ „
4·4	14·5 „	57·0 „	400 „ „
4·5	16·0 „	33·0 „	100 „ „

Fig. 2.



After completing a series of explosions with moist gases several hours evacuation and several explosions with dry gases were necessary in order to dry the bomb. During the drying process, increasing deflexions were always recorded which finally reached a steady value. Similarly upon introducing wet gas into the dry bomb the deflexion did not at once drop to the normal value for the moist gases owing to absorption of moisture by walls of the bomb. Fig. 2 shows the complete spectrum for the dried gases. During this series the experimental conditions were maintained as constant as

possible. After each explosion the bomb was evacuated for one hour and subsequently washed out with a definite small quantity of the dried gaseous mixture. The bomb was again evacuated before filling with the mixture to a pressure of 75 cm. ; the gas passed through about 50 cm. of P_2O_5 on its way to the bomb and remained in contact with the drying agent for an hour. No estimation has yet been made of the actual moisture-content after drying, but occasionally the mixture failed to fire.

It will be noticed (fig. 2) that, in contrast to the results recorded in the table, the ratio of the intensities at the two maxima in the explosion of moist gases has been maintained in the explosion curve for the dried gas mixture. It is certain that the bomb was more thoroughly dried before taking the complete spectrum than in the preliminary work. It would seem, therefore, that the emission at the maximum at 2·8 μ is more sensitive to traces of water than that at 4·4 μ, and is more readily suppressed.

In order to test if the increased intensities obtained on drying were due to absorption by water vapour in front of the wave, the absorption of the wet and dry gas mixtures was measured. This was tested in a small glass cell, 10·7 cm. long and 1 cm. wide, with fluorite windows. The fluorite was perfectly clear and its transparency to infra-red radiation proved by test. Le Page's fish-glue served as cement for the windows. The Meker burner was used as a source of infra-red radiation. The mean values of a large number of determinations for various wave-lengths are given for the empty cell, and the cell filled with the wet and dry mixture respectively at 75 cm. and 20° C.

μ.	Deflexion. Empty Cell.	Cell + Dry Gases.	Cell + Wet Gases.	Per cent. Absorption.
2·4	2·3 cm.	2·1	2·1	8 per cent.
2·8	4·7 „	4·8	4·5	6 „ „ wet 0 „ „ dry
4·4	15·0 „	11·3	11·2	25 „ „
4·5	14·7 „	9·9	9·9	33 „ „
4·6	11·1 „	6·3	6·3	43 „ „

The results may be considered accurate to within 2 or 3 per cent. Except at 2·8 μ, the absorption was the same for both wet and dry mixtures. These experiments also showed that the presence of water vapour did not influence the magnitude of the reflexion from windows and walls of

the cell. These results are in agreement with the measurements of Hettner (*Ann. Phys.* lv. p. 496, 1918), who finds that water vapour does not absorb so strongly as liquid water. At 4·4 μ he found that the absorption by 100 cm. of vapour at 100° C. and atmospheric pressure was zero.

The possibility that the decrease in intensity on addition of water is due to complex formation between carbon monoxide and water is also eliminated.

Total Infra-red Emission.

The relative intensities of the total infra-red emission were measured for explosions of both the dry and the moist gaseous mixtures. The gases were dried by the method described above. The ratio of the deflexions obtained was 2·5 : 1, the dry gas giving the higher emission. The addition of 2–3 per cent. of hydrogen to the dried gas mixture gives a similar result.

Haslam, Lovell, and Hunneman (*loc. cit.*) have measured the percentage of the chemical energy which is radiated from the carbon monoxide flame. This is 10·4 per cent. for a gaseous mixture not specially dried. Thus on drying the gases the increase in the percentage of the heat of reaction which is emitted as radiation may well be of the order of 15 per cent. The loss of so much energy by radiation in the explosion of the dried gases would very materially influence the rate of rise in temperature of the gases in the explosion wave.

Use of the Thermopile for Measurements of Radiant Energy from Explosions.

Two series of experiments were carried out ; in the first, constant small amounts of radiation were allowed to fall upon the thermopile over different intervals of time ranging from one fiftieth of a second to one second, and in the second, radiation from a constant source fell upon the thermopile for different time periods. The experiments showed (1) that in agreement with theory, if a given small amount of energy falls upon the thermopile over different time intervals, the shorter the time the greater is the deflexion ; (2) the arrangement acts ballistically provided the time over which the radiation is received by the thermopile does not much exceed 0·2 second.

In the case of the explosion of the moist gases where condition (2) holds, the curve, when corrected for absorption in front of the wave, gives a good representation of the

distribution of energy in the spectrum. The time during which radiation is emitted is longer for the dry than for the wet mixture ; in this case the action may not be ballistic. The correction to be applied is of such a nature that the differences between the intensity of radiation from the moist and dried mixtures would be materially augmented. This correction has not been made to fig. 2 since at present the explosion times of the moist and dried mixture have not been measured. Factors such as the absorption by water vapour, contamination of the window, and reflexion from the walls of the bomb have been considered in relation to the phenomena described. It has been shown that water vapour does not absorb appreciably in the regions where the effect is most marked. Neither are absorbing complexes formed when water vapour is added to carbon monoxide and oxygen mixture at ordinary temperatures. Contamination of the window has been disproved by the fact that after explosions of moist gases mere pumping out will ultimately bring the deflexion back to the value for dried gas. The results obtained in experiments upon the absorption of moist and dried gas mixtures rule out reflexion from the walls as a disturbing factor. The energy changes involved in the dissociation of water vapour at the explosion temperature have been shown by calculation to be totally inadequate to account for the very large changes in the emission intensity.

Perhaps the most convincing evidence for the theory of energo-thermic catalysis, water being regarded as a positive catalyst, has been obtained during the study of the effects of certain vapours, such as ethyl nitrate and carbon tetrachloride, upon the radiation from explosions of carbon monoxide and oxygen. This will be described in a subsequent paper.

The Carbon Monoxide Flame.

The only comprehensive investigation of infra-red flame spectra which has been carried out up to the present time is that of Julius (*Verhandl. des Vereins zur Beforderung des Gewerb fliesses im Preussen*, lxviii., 1889). In particular he mapped the carbon monoxide flame and showed that it possessed two characteristic maxima. Unfortunately his values for the dispersion of rock-salt were taken from Langley; later work by Rubens proved that Langley's calibration was unsound, and that the wave-lengths recorded by Julius were too large sometimes by more than $0{\cdot}1\,\mu$. In view of these inaccuracies it was desirable that a new

determination of the infra-red spectrum of the carbon monoxide flame be made. This has been done for the purposes of comparison with the explosion spectrum.

The flame of dry carbon monoxide burning in dry oxygen has been studied and the two maxima mapped. The burner employed was a small quartz jet with an orifice 3 mm. in diameter, and the two gases were admitted into this at measured rates; the flame was about 0·5 cm. broad and 1·5 cm. high. As the flame was not enclosed, atmospheric moisture may have affected the dry flame to some extent, but a preliminary experiment showed that the difference in the water-content of the two flames was sufficient to give rise to markedly different rates of burning. The complete spectrum for the moist flame is given in fig. 1 and, as for the explosion curve, no correction is made for the change of dispersion of rock-salt over these spectral regions.

Although the rate of burning of the gases in the dry flame was slower than in the moist flame, the ratio of the intensities for the 4·4 and 2·8 μ bands was practically the same in both flames, *e.g.* 10 : 1 (Julius gives 14 : 1). Many readings were taken at different times and this ratio was constantly obtained; but occasionally ratios greater than 10 : 1 were recorded, ranging between 11 : 1 and 15 : 1 with the dry flame. Examination of the flame spectrum reveals that both maxima have been shifted towards the shorter wave-lengths by about 0·03 μ when compared with the spectrum of the Meker burner. This indicates a low mean flame temperature (Paschen and Coblentz, *loc. cit.*). The regions in the neighbourhood of 2 μ and 14 μ were examined but no emission was found. The sensitivity was such that an intensity one fiftieth that at 4·4 μ could have been detected.

The addition of 15 per cent. by volume of hydrogen to the gas mixture raised the flame temperature, bringing the 4·4 μ maximum back to its normal position and producing a corresponding decrease in the ratio of the intensities of the two bands. The hydrogen-carbon monoxide flame is thus very similar to the coal-gas flame.

Summary.

The infra-red spectrum of carbon monoxide burning in oxygen has been mapped for the flame and for the explosion between 1·3 and 6·1 μ. Experiments have been described illustrating the remarkable influence of small quantities of

water vapour in depressing the emission of infra-red radiation from the explosion, which is accompanied by a corresponding increase in the rate of reaction. The action of water is a special case of a general phenomenon, and a theory involving a new type of catalysis has been propounded in order to explain the experimental results.

The term *energo-thermic* catalysis is proposed for the action of those substances which retard or accelerate the rate of attainment of thermal equilibrium in a reacting gaseous mixture.

We wish to express our indebtedness to Dr. S. W. Saunders for many valuable suggestions, to Brunner, Mond & Co. for a grant for the purchase of the spectrometers and galvanometers used in the research, and to the Department of Scientific and Industrial Research for a personal grant to one of us (C. H. J.).

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X. *Note on some Band Spectra associated with Silicon.* *By* W. H. B. Cameron, *M.Sc., Research Student, Queen's University, Belfast* *.

[Plate III.]

IT might be expected that silicon, which has an electron structure similar to that of carbon, should show some analogy with the latter element in the production of band spectra from its compounds. An attempt has been made to test whether the analogy holds, and, although circumstances did not permit of an exhaustive search being made, such results as have been obtained are here briefly recorded.

Amongst the better known and more easily obtainable spectra of carbon are those which have been attributed to its compounds with nitrogen, hydrogen, and oxygen, several band systems in many cases having their origin in the same carrier.

Jevons has recorded two band spectra which he has attributed to the nitride † and chloride ‡ of silicon, and has

* Communicated by R. C. Johnson, B.A., Ph.D.
† Proc. Roy. Soc. A, lxxxix. p. 187 (1913).
‡ Proc. Roy. Soc. A, cvi. p. 174 (1924).

assigned a third system, which had been observed previously by de Gramont and de Watteville *, to the oxide. So far as the author is aware, no other band systems of silicon are known, with the exception of the silicon fluoride bands investigated by Porlezza †.

Two methods, which have proved very effective in producing the Swan bands of carbon have been tried ‡ in the case of silicon to produce the analogue of this spectrum.

(1) An arc has been burned in a slow stream of hydrogen at a pressure of about 6 or 7 mm. of mercury. The silicon (which was supplied in lumps, and could only be obtained in a commercially pure state) quickly became covered with a dark-coloured coating of non-conducting material, but no band spectrum was recorded on the photographic plate.

(2) A discharge tube of the ordinary pattern was furnished with silicon electrodes gripped by aluminium wire. In addition there were the usual bulbs containing KOH and P_2O_5 for the removal of carbon gases and of water vapour, and a palladium regulator to allow of admission of hydrogen. After cleaning, the tube was filled with argon at a pressure of 10–12 mm. of mercury, and hydrogen was admitted. No trace of any band spectrum was observed, although there were several groups of silicon lines in evidence.

An attempt to produce the silicon oxide bands in a similar tube containing pure oxygen at a pressure of less than 1 mm. of mercury was equally unsuccessful, no system being observed other than the negative and ultra-violet bands of oxygen.

When an arc is burned between silicon poles in air or in oxygen at atmospheric pressure, the light is of a whitish colour, and a photograph taken on a quartz prism instrument shows the silicon oxide bands mentioned above together with many lines. This is akin to one of the methods § used by Jevons in developing the system, when he burned an arc between carbon poles packed with silica or with crushed silicon. An interesting observation was made when the silicon arc was burned in a slow stream of oxygen at a pressure of about 10 mm. of mercury. The light then became an intense blue colour, and in addition to a good development of the silicon oxide bands being shown, a system of 5 or 6 bands appeared in the blue region of

* *Comptes Rendus*, cxlvii. p. 239 (1908).
† *Rend. Accad. Linc.* (V.), xx. 2nd half-year, p. 488.
‡ 'Nature,' Oct. 10, 1925 (Letter).
§ *Loc. cit.* (1924).

the spectrum. A strong condensation of somewhat complex structure invariably accompanied this system. In appearance it was almost like an isolated band degraded to the red with head at about λ 4214. This system was also developed under similar conditions when air was substituted for oxygen, but in this case the development was much weaker. The silicon poles quickly became covered with a heavy deposit of silica, and the arc ceased to burn after about 15 or 20 seconds. The conditions of excitation of this system would seem to point to an origin in some silicon oxide molecule, and it was hoped that by arranging the system in series, it would be possible to relate it to the known silicon oxide bands. The bands, which are degraded to the red and occur in pairs, presented some difficulty as regards measurement, owing to the superposition of continuous spectrum together with some lines. The wave-lengths are given in Table I., but the accuracy is not guaranteed to more than

Table I.

λ.		Int.		Remarks.
4393·4	.....	2		
4408·9	.....	5	.....	May be line superposed.
4417·5	.....	2	.....	Possible position of second head.
4454·2	.....	3		
4466·3	.....	4	.....	May be line superposed
4474·6	.....	2	.....	Possible position of second head.
4516·1	.....	3		
4525·6	.....	3		
4577·1	.....	2		
4585·0	.....	1		
4637·1	.....	1	.....	Position doubtful.
4648·2	.....	1	.....	,, ,,

1 Ångström unit, although in the greater proportion of the bands it is probably much better. Since only one sequence has been identified with certainty, it has not been found possible to relate this system to any other.

Owing to the fact that silicon could not be obtained in a chemically pure state, there still remains the possibility that the system in question arises from some impurity in the silicon poles. This is supported by the fact that the blue system is not developed when carbon poles, packed with pure precipitated silica, are substituted for the silicon poles, although the known silicon oxide bands are present. Carbon poles packed with crushed silicon permit of the development of the blue system.

In his paper, "On the Spectrum of elementary Silicon"*, Sir William Crookes stated that a sample of comparatively pure silicon showed on analysis that the main impurities were titanium, iron, and aluminium. In addition, we have found in our samples spectroscopic evidence of the presence of copper and manganese. Arcs have been burned in low pressure oxygen between poles of iron, aluminium, and brass, and also between carbon poles packed with titanium dioxide and manganese dioxide, but in no case has the blue system appeared. The ideal test, of course, would be to burn an arc between poles of pure silicon if such could be obtained.

It is suggested that this blue system, of which a photograph is given in Plate III. *a*, has its origin in a silicon oxide molecule.

Jevons has recorded that he obtained a good development of the silicon oxide bands by passing an uncondensed discharge through the vapour of silicon tetrachloride in the presence of oxygen. The writer has not been able to reproduce the system by this method, a fairly strong continuous spectrum being invariably present in the region occupied by the silicon oxide bands. It was noticed that when the vapour of $SiCl_4$ was pumped through the discharge tube at very low pressure, and oxygen added in slight excess, the colour of the discharge became dark green. When examined with a small direct-vision spectroscope this showed a closely spaced series of narrow bands extending almost throughout the entire visible region. The bands apparently occurred in pairs and were strongest in the green and blue regions. Photographs were obtained on a glass prism instrument having a dispersion of 3·2 ins. from λλ 7000–3900, exposures of about 2½–3 hours being required. These photographs showed that the bands were degraded to the red, and in many cases the fine structure was clearly developed to a considerable distance from the head. This caused much overlapping, which, in addition to the presence of several lines, rendered the identification of some of the band heads very difficult. A few bands degraded in the opposite direction were also observed.

During the course of the experiment, a grey deposit of silica accumulated on the walls of the discharge tube.

A photograph of this spectrum has been reproduced, and is shown on Plate III. *b*. Wave-lengths of the heads of these bands are given in Table II., but again an accuracy greater than 1 Ångström unit is not claimed owing to the difficulties of measurement.

* Proc. Roy. Soc. A, xc. p. 512 (1914).

TABLE II.

λ.	Int.	Remarks.
3960·2	0	Very faint.
3979·2	0	,, ,,
4007·3	0	,, ,,
4015·8	0	,, ,,
4033·3	0	,, ,,
4042·1	0	,, ,,
4059·8	0	Degraded to violet.
4072·2	0	Confused with line.
4083·4	0	
4093·2	0	
4113·1	1	
4120·7	0	
4140·1	1	
4147·6	0	
4171·4	0	Doubtful.
4178·8	1	
4190·4	0	Degraded to violet.
4191·2	0	Line?
4195·2	2	Line superposed.
4197·0	1	
4217·3	1	
4232·8	1	
4238·7	1	Line?
4245·6	1	Line?
4248·7	1	Doubtful.
4252·7	1	
4286·3	1	
4291·5	1	Line?
4317·4	2	Line superposed.
4319·6	1	
4349·1	2	
4381·2	2	
4390·0	7	Line superposed.
4404·9	1	
4421·2	1	
4441·5	1	
4487·8	3	
4506·9	2	
4510·5	1	Line?
4552·3	4	
4586·3	3	Degraded to violet.
4614·2	3	
4655·8	2	
4683·1	3	
4751·6	3	
4795·0	6	Line superposed.
4852·8	1	
4870·9	1	
4925·1	1	
4942·5	1	
4977·3	2	
5078·4	4	Position somewhat doubtful.
5397·0	2	,, ,, ,,
5506·1	0	,, ,, ,,
5677·6	1	,, ,, ,,

Throughout the greater part of the spectrum, as obtained by the glass prism spectrograph, the grouping of the bands

in pairs (which was evident in the case of low dispersion observations) is not at all apparent, and it is very difficult to decide whether or not the grouping is genuine. Again, several of the bands seem to show a minor doublet separation in the head, but whether this is to be ascribed to the presence of Q branches, or to the isotope effect, or to the superposition of a faint line near the head of the band, is not quite clear.

It is now well established that 5 band systems have their origins in the neutral CO molecule, and 3 in the singly ionized CO molecule. In the case of silicon oxide, there are considerably fewer band spectra known and the relationship between these is at present obscure. It is possible that the silicon oxide bands observed by de Gramont and de Watteville and investigated by Jevons, are the analogue of the 4th positive carbon bands, and it is suggested tentatively that the bands recorded in Table II. may be the analogue of the comet-tail and associated bands of CO. Before these matters could be definitely settled, however, it would be necessary to obtain photographs under more ideal conditions, and to make a more accurate determination of wave-lengths.

I wish to express my sincere thanks to Dr. R. C. Johnson, whose advice and help were much appreciated.

Description of the Plate.

PLATE III. *a*.—Bands in the blue region of the spectrum, obtained by burning an arc between silicon poles in oxygen at about 10 mm. pressure.

PLATE III. *b*.—Bands obtained by passing an uncondensed discharge through the vapour of silicon tetrachloride at very low pressure, with oxygen added in slight excess.

XI. *The Passage of Positively-charged Particles through Helium.* *By* A. J. DEMPSTER, *Ph.D., Associate Professor of Physics, University of Chicago* *.

IN the course of experiments on positive-ray analysis it was observed that the rays could often be detected when considerable gas was in the apparatus. The rays apparently maintained their positive charge even after several collisions. The passage of α-rays through atoms has led to important conclusions concerning atomic structure; further study has recently shown that the α-particles capture and lose electrons

* Communicated by the Author.

along their path*, and alternate between a doubly- and singly-charged condition. The free path for the capture of an electron has been found to decrease rapidly as the velocity decreases †. In the ordinary canal rays we have charged particles of an intermediate velocity acquired by falling through several thousand volts. The phenomenon of alternation of charge with these rays have been studied in several investigations ‡. Rüchardt § has found that the free path for neutralization of protons or positively-charged hydrogen atoms accelerated by 13,000 to 16,000 volts is slightly less than the free path between collisions in the kinetic theory of gases.

In the present paper very slow rays are studied that have obtained their velocity by falling through 14 to 1000 volts potential difference. From the results of investigations with faster rays we might expect that these charged particles would always be neutralized very rapidly.

The apparatus used is illustrated in fig. 1. It is the same as that used for the analysis of charged particles of different masses. The source of the ions was a cold lithium anode that was bombarded by electrons of about 120 volts velocity from a hot cathode. It had been noticed in previous work that charged hydrogen atoms or protons were obtained from an anode filled with metallic lithium, probably coming from a layer of hydroxide on the surface. At the same time, hydrogen molecule ions were obtained as well as heavier ions that were probably charged water molecules and carbon-monoxide ions. When helium was introduced, singly-charged helium atoms were also obtained. The ions passed through an opening into the main accelerating chamber, where various potentials were applied. A slit S_1 then separated out a narrow bundle that was deflected by a magnetic field so as to fall on an electrode connected to a string electrometer. The total path covered by the ions was 17 cm.

Helium was allowed to flow through a fine capillary tube into the apparatus from a reservoir whose pressure could be varied. By keeping the mercury pump running, various pressures could be established in the apparatus. The pressures were measured by a McLeod gauge that was joined

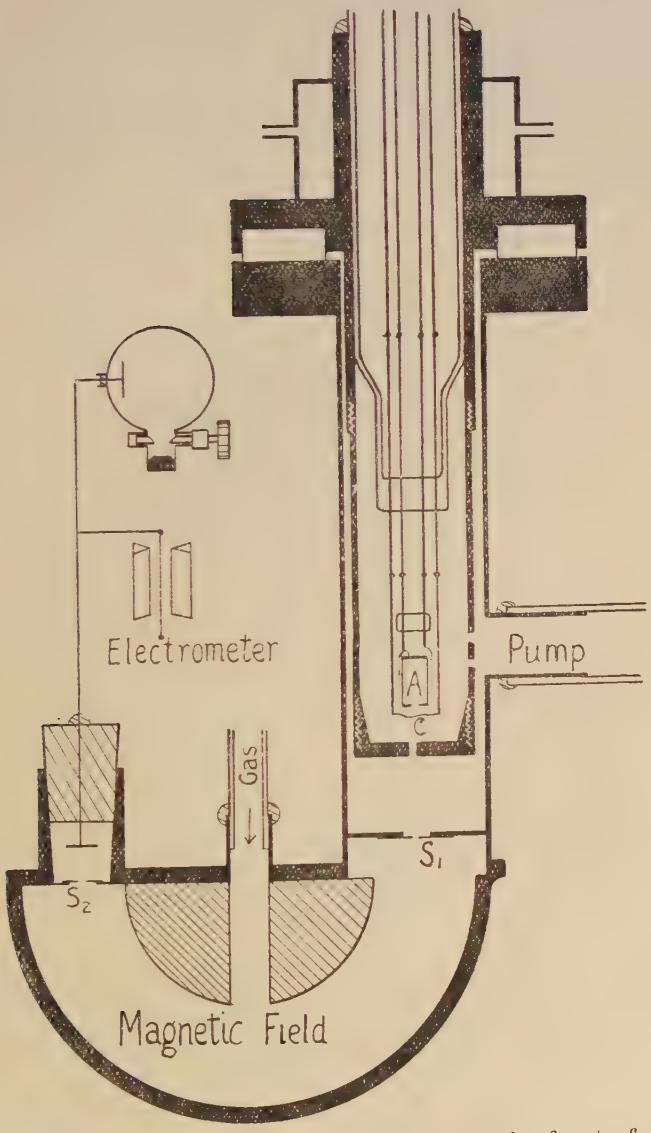
* Henderson, Proc. Roy. Soc. A, cii. p. 496 (1922).

† Rutherford, Phil. Mag. xlvii. p. 277 (1924).

‡ J. J. Thomson, 'Rays of Positive Electricity,' pp. 46–53. W. Wein, *Kanalstrahlen*, pp. 134–167.

§ E. Rüchardt, *Annalen der Physik*, lxxi. p. 380 (1923); lxxiii. p. 230 (1924).

Fig. 1.

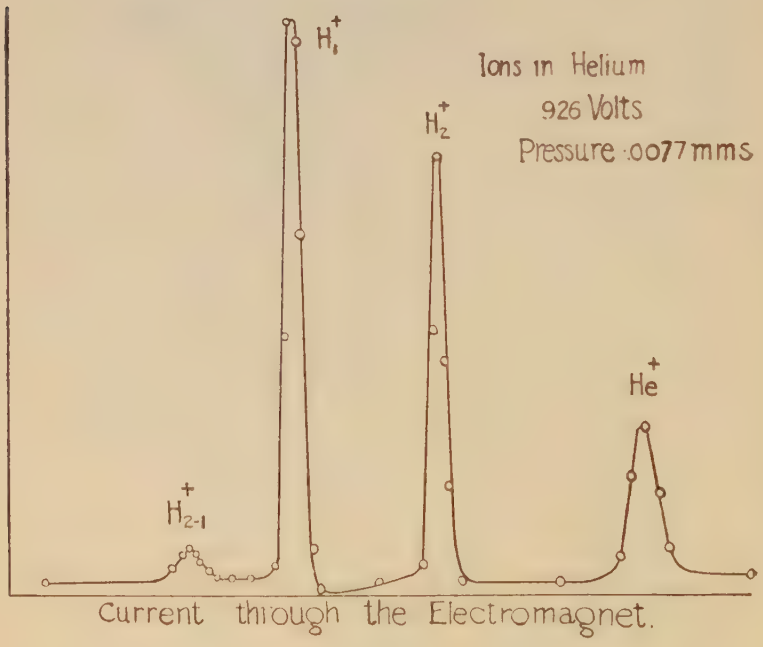


to the inflow tube about twelve centimetres in front of the apparatus. The pressure gradient in this length of tubing, which may amount to an appreciable error with rapid pumping, was eliminated later by means of pressure

measurements made with a connexion directly to the chamber.

The currents obtained with 926 volt rays as the magnetic field was increased so as to bring various ions on to the second slit are shown in fig. 2. The relative masses of the rays H^+_1, H^+_2, and He^+ could be obtained from the accelerating voltages necessary to bring them on to the second slit

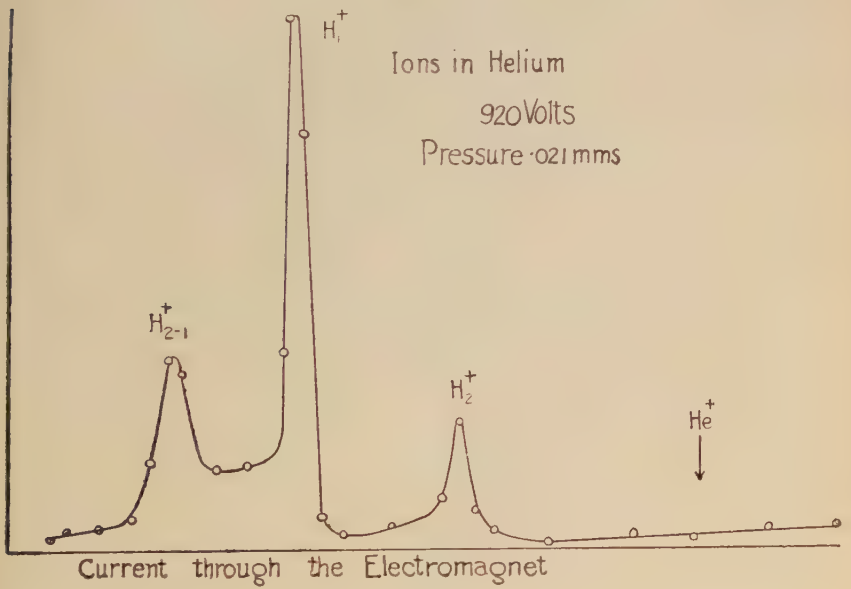
Fig. 2.



with constant magnetic field. The absolute values could be found approximately from the strength of the magnetic field, and verified by the disappearance of He^+ when no helium gas was present. When helium is introduced to a pressure of ·0077 mm. of mercury, two new maxima appear that are not present at zero pressure—He^+ and a small maximum marked H^+_{2-1} in fig. 2. The latter is probably due to ions that have been accelerated as charged hydrogen molecules and then dissociated into a neutral atom and a charged hydrogen atom that is strongly deflected on account of its slow velocity.

Such rays have been observed by J. J. Thomson * and H. D. Smythe †. It is significant that the process of dissociation does not prevent the atoms formed from continuing on in the same direction with the original velocity. If we consider the helium atom to have the cross-section given by the kinetic theory of gases, and the proton to be a rapidly-moving mass of very small dimensions, we find that the proton makes 1·6 collisions with the pressure in fig. 2 in completing the path of 17 cm. The number of collisions for the other ions would be correspondingly greater.

Fig. 3.



With a helium pressure of ·021 mm., in which the protons would make 4·8 collisions, the curve in fig. 3 was obtained. The helium ions have all been neutralized before reaching the second slit, and the hydrogen molecule ions are much weakened in comparison with the protons. Their disappearance is accompanied by an increase in the bundle of

* J. J. Thomson, 'Rays of Positive Electricity,' pp. 63–67.
† H. D. Smythe, Phys. Rev. xxv. p. 452 (1925).

dissociated protons H^+_{2-1}. Fig. 4 shows the rays at a still higher pressure. Here the protons make 11 collisions in

Fig. 4

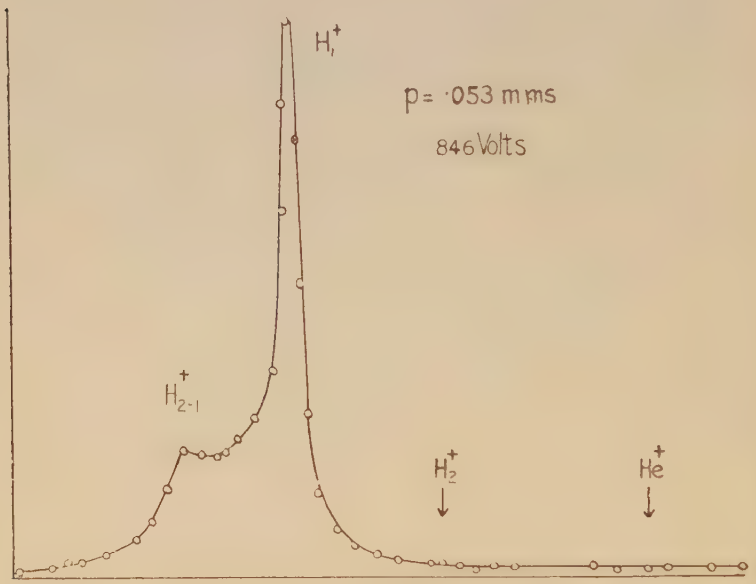
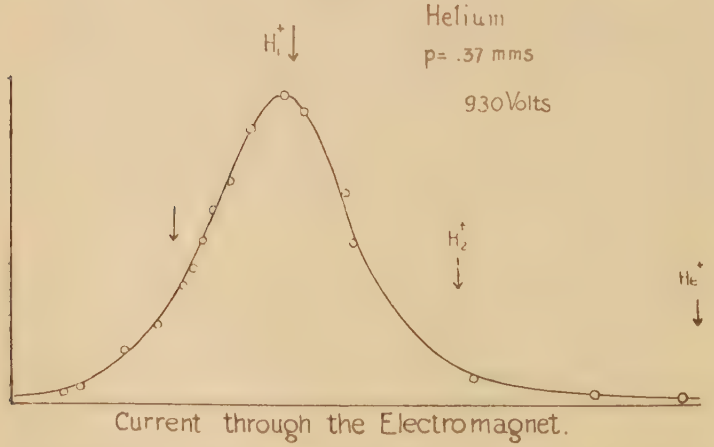


Fig 5..



the path completed. The hydrogen molecule ions have disappeared. As the pressure is increased still further, the bundle of protons becomes broader. Fig. 5 shows the

broadened bundle at 0·37 mm., where 80 collisions are made. A similar bundle was observed up to pressures of 0·467 mm., where arcing occurred. The kinetic theory value for the free path of a rapidly-moving particle is 1·58 mm. at this pressure, giving 108 collisions for the protons in the path completed. The rays are seen to be considerably broadened as a result of their passage through the atoms.

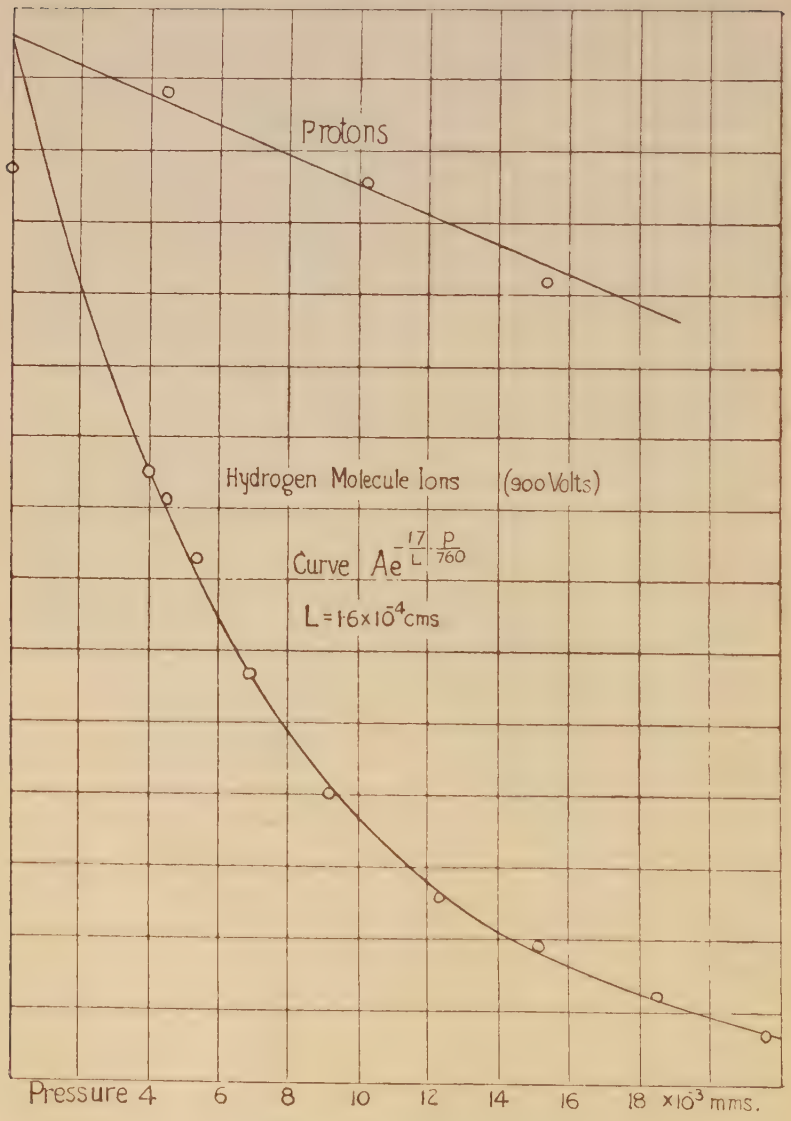
Similar results were obtained with lower potentials, although the rays were weaker, due to increased broadening and to the fact that a smaller proportion will pass through a slit at low velocities. By removing the plate between the cathode and main accelerating chamber, protons were obtained with potential differences as low as 14 volts between the anode and the first slit. These were observed with helium pressures up to 0·03 mm., at which pressure the protons would make five collisions in the path completed.

Experiments were made to observe the rate of neutralization of the helium ions and the rate of dissociation of the hydrogen molecule ions. Fig. 6 shows the intensity of the maximum of the hydrogen molecule ions accelerated by 900 volts as the pressure was increased. The bombarding current was kept constant, and we may attribute the decrease of intensity to dissociation of the rays. A decrease of the intensity of the maximum would also be caused by the broadening of the bundle. This latter appears to be the chief cause affecting the bundle of protons, and its effect at low pressures is given by the curve at the top of fig. 6. Since this small current decrease due to scattering would be still less in the case of heavier ions, provided they actually penetrated the atoms, we shall neglect it and attribute the decrease in intensity entirely to dissociation of the positively-charged particles. The observations agree well with a theoretical curve $Ae^{-\cdot 139p}$, giving a free path for dissociation of the hydrogen molecule ions in helium of $1\cdot61\times10^{-4}$ cm. when reduced to atmospheric pressure. This is about 9·4 times the kinetic theory free path in helium.

In a preliminary experiment with slower rays (340 volts) a still longer free path was obtained, indicating a dependence of the rate of dissociation on the relative velocity of the particles.

The intensity of the singly-charged helium ions obtained at different pressures of helium is shown in fig. 7. The ionizing current from the cathode to the anode was maintained constant. With the pressures used the number of ions formed would be proportional to the pressure. The decrease of the currents at high pressures may be attributed

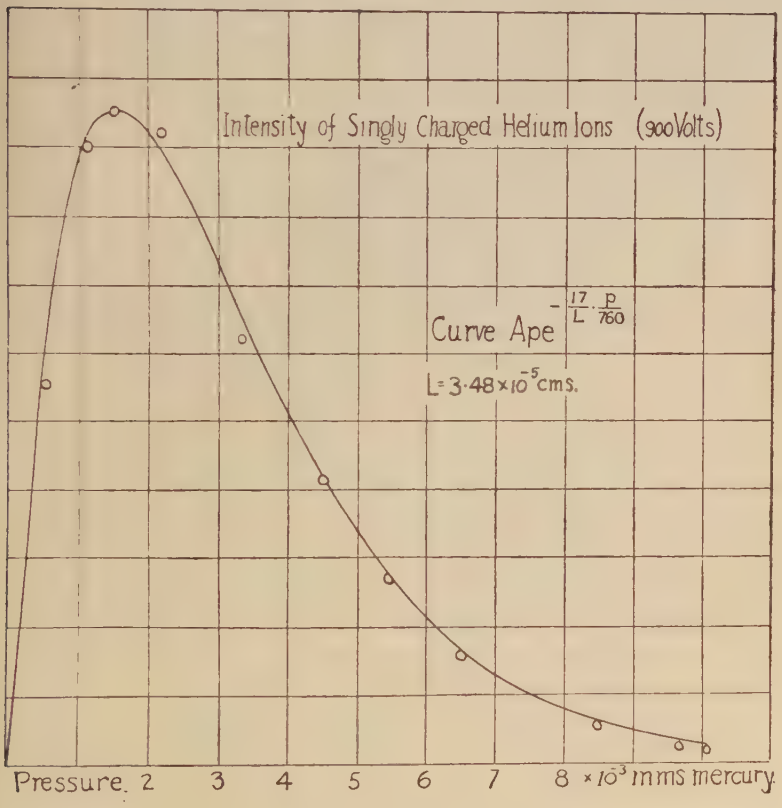
Fig. 6.


Protons
Hydrogen Molecule Ions (900 Volts)
Curve $Ae^{-\frac{17}{L}\frac{P}{760}}$
$L = 1{\cdot}6 \times 10^{-4}$ cms
Pressure 4 6 8 10 12 14 16 18 $\times 10^{-3}$ mms.

either to neutralization or to deflexion of the ions out of the beam. With hydrogen the appearance of atoms showed that the molecule ions decreased because of dissociation.

The hydrogen molecule ions, however, were able to maintain their structure, velocity, and direction after many kinetic theory collisions. From the general similarity of structure we should also expect large-angle deflexions at collisions to be absent in the case of the helium ions, and the weakening of the rays to be due to neutralization. If L is the

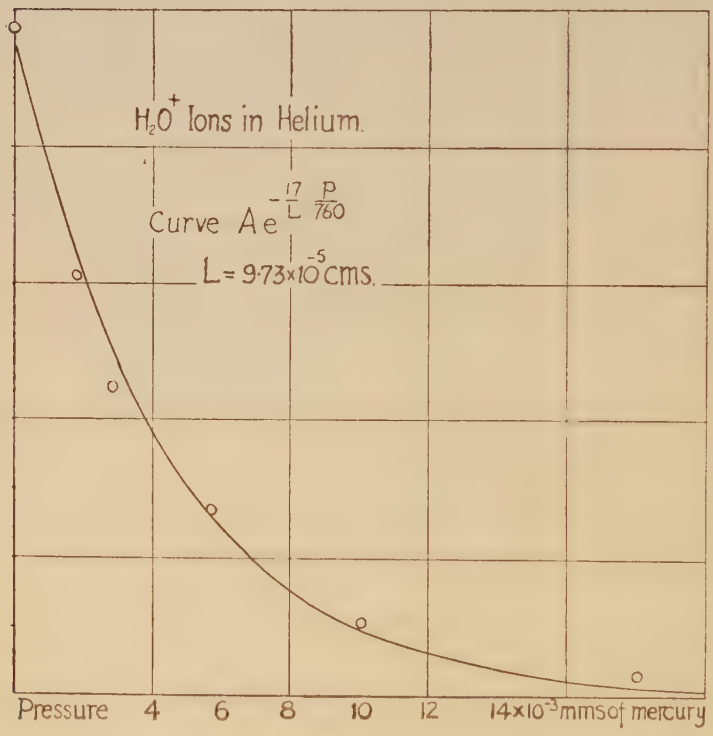
Fig. 7.


Intensity of Singly Charged Helium Ions (900Volts)
Curve Ape $^{-\frac{17}{L}\cdot\frac{p}{760}}$
L=3·48×10^{-5}cms.
Pressure. 2 3 4 5 6 7 8 ×10^{-3} mms mercury

mean free path for neutralization at atmospheric pressure and p is the pressure in millimetres of mercury, the number of charged particles remaining after 17 centimetres is given by the expression $Ape^{-\frac{17}{L}\cdot\frac{p}{760}}$. The curve in fig. 7 is drawn for $L=3{\cdot}48\times10^{-5}$ centimetre, and the agreement with the observations is very satisfactory. The free path differs very little from the free path given by the kinetic gas theory; in

fact, if we assume the ion diameter to be the same as the atomic diameter, the ion would make on the average only 1·4 collisions before neutralization. The disappearance of water-vapour ions with pressure is given in fig. 8. Here the free path for neutralization is $9{\cdot}7 \times 10^{-5}$ centimetre for particles accelerated by 936 volts. This is several times the kinetic theory free path. The rate at which the different ions disappear appears to be dependent on the type of ion.

Fig. 8.



At very low velocities the phenomena are probably quite different, since for ordinary ions in gases we have satisfactory theories based on the same kind of collisions as in the kinetic gas theory.

In distinction to the ions just mentioned, the bundle of protons of the speeds used showed no decrease in total intensity as the helium pressure was increased. The maximum decreased, but this could be attributed to broadening of the bundle. The protons appeared to pass freely through

the atoms of helium without neutralization and with only slight changes in velocity or direction. Many experiments were made to see if there was any decrease in the velocity of the protons in their passage through the atoms. If any loss occurred, a slightly higher accelerating voltage would be necessary to keep the rays on the second slit when the helium was introduced. When helium containing traces of hydrogen was used, protons were obtained, at the higher pressures, from ionization of the hydrogen impurity. These rays gave a bundle that had a slower velocity, since they fell through only part of the field where they were made. However, when the hydrogen was removed so that only protons from the anode were obtained, the setting on the maximum of the 900-volt protons from the anode with and without helium present was almost identical. With a helium pressure that gave 17 collisions for the protons, the increase in the accelerating potential required to keep the maximum on the slit varied from zero to ten volts. We may thus conclude that if the proton loses any energy in penetrating the atom, it is probably less than that corresponding to half a volt per collision.

There is evidently considerable broadening of the beam of protons. G. P. Thomson * has measured the scattering of protons with higher velocity, and found that it was considerably greater than might be expected. It has not been found possible as yet to draw definite conclusions from the curves obtained in these experiments as to the magnitude of the scattering of the slow protons by the atomic fields of force. Experiments with a different arrangement may yield more definite results.

The rapid neutralization of protons observed in canal rays of high velocity and the capture of electrons by α-rays have been discussed theoretically by Rüchardt † and Fowler ‡. Both theories suppose electrons to be present that are free to combine with the moving nucleus. The slower the nucleus the more likely is the capture of an electron to take place. From this point of view we are led to conclude that protons of the speed used in these experiments are unable to produce free electrons by ionizing the helium atoms. That fast protons are unable to ionize is shown, however, by Blackett's § drop-track experiments. The absence of ionization by slow

* G. P. Thomson, Proc. Roy. Soc. A, cii. p. 197 (1922); Phil. Mag. June 1926.

† E. Rüchardt, *Zeitschrift für Physik*, xv. p. 164 (1923).

‡ R. H. Fowler, Phil. Mag. xlvii. p. 416 (1924).

§ P. M. S. Blackett, Proc. Roy. Soc. cvii. p. 349 (1925).

protons may be interpreted in several ways. J. J. Thomson * has pointed out that the energy transferred to an electron by the impact of a proton is only a small fraction of the energy of the larger mass. These mechanical considerations may have to be modified if we admit the possibility of the production of excited atomic states and the transformation of this energy into kinetic energy of the electron. A discussion of the bearing of these processes on the ionization potential of positive ions has been given by Franck †.

A second point of view was suggested by J. J. Thomson ‡ to explain the ionization found by many observers when gases are bombarded by ions from hot salts. If the ion is moving with sufficient velocity to pass through the neutral molecule, it may be able to capture an electron and so leave a gas ion behind. Franck § has interpreted the change of the charge of the canal rays at collisions in this way using the concept of electron affinity. On this point of view we could explain the failure of the proton to capture an electron during its passage through the atom by the fact that the ionization potential of helium is 24·5 volts, while the energy of formation of a neutral hydrogen atom is only 13·6 volts. There is thus no tendency for an electron to leave the helium atom in order to join with the hydrogen nucleus.

The protons used in these experiments have much slower velocities than the electrons in the helium atom, so that the modification of the electronic orbits as the proton passes through the atom is brought about and disappears very gradually. The ionization produced by rapidly-moving protons in ordinary canal ray experiments, or in Blackett's experiments, may occur when this slow adjustment of the electronic orbits to the new electric forces is no longer possible.

Slow electrons that have fallen through potential differences of a volt or less have recently been found to have long free paths in the rare gases ‖. The character of the interaction of a charged particle with an atom must depend primarily on the electric forces involved and their rates of variation, rather than on the mass of the charged particle. We should thus expect protons to exhibit analogous properties to slow electrons

* J. J. Thomson, 'Rays of Positive Electricity,' 2nd Ed. pp. 56–59.

† Franck, *Zeitschrift für Physik*, xxv. p. 312 (1924).

‡ J. J. Thomson, 'Rays of Positive Electricity,' 2nd. Ed. p. 59.

§ J. Franck, *Physikalische Zeitschrift*, xiv. p. 623 (1923).

‖ H. F. Mayer, *Annalen der Physik*, lxiv. p. 451 (1921). C. Ramsauer, *Annalen der Physik*, lxiv. p. 513 (1921), lxvi. p. 546 (1922). J. S. Townsend and V. A. Bailey, Phil. Mag. xliii. p. 593 (1922).

when they move with the same velocities *. The velocity of the protons used in these experiments, $5{\cdot}3 \times 10^6$ to 44×10^6 cm. per second, is acquired by an electron in falling through only ·01 to ·5 volt, so that these protons have velocities for which electrons possess long free paths. Experimentally the larger mass makes it more convenient to work with protons than with electrons of these speeds.

The writer's thanks are due to Mr. G. E. Read for assistance in making observations.

Summary.

Protons with velocities corresponding to potential differences of 14 to 900 volts pass through many helium atoms without neutralization, and with only slight changes in velocity or direction.

Hydrogen molecule ions are dissociated with a free path for dissociation about 9 times the kinetic theory free path for 900-volt rays.

Helium ions are neutralized at about the first collision.

Ryerson Physical Laboratory,
University of Chicago.
June 1920.

XII. *Electricity in Flames.* *By* James A. J. Bennett, *M.A., B.Sc., William Houldsworth Research Student and Carnegie Research Scholar, University of Glasgow* †.

Contents.

Part I.—Electrical Conductivity of Flames containing Alkali Salt Vapours.

Part II.—The Thermal Ionization of Gaseous Elements at High Temperatures—a confirmation of the Saha Theory.

Part III.—Velocity of Electrons in a Bunsen Flame.

Part I.

Electrical Conductivity of Flames containing Alkali Salt Vapours.

Introduction.

THE main object of the experiments described in this paper was to find how the electrical conductivity of a Bunsen flame containing alkali salt vapours varies with the temperature.

* A. J. Dempster, Proc. of the Nat. Acad. Sci. xi. p. 552 (1925). G. P. Thomson, 'Nature,' Feb. 13 (1926).

† Communicated by Prof. E. Taylor Jones, D.Sc., F.Inst.P.

The temperature of the flame was varied by altering the gas supply and by the addition of carbon dioxide. Many papers on the conductivity of salt vapours in flames have been published, but the effect of the temperature of the flame on the conductivity has not hitherto been investigated.

The variation of the electrical conductivity of flames containing salt vapours with the concentration of the salt vapours in the flames has been investigated by H. A. Wilson (Phil. Trans. A, p. 63 (1915)), who found that the variation of the conductivity (c) with the concentration (k) for alkali salts can be represented by the equation

$$\frac{kc}{c^2-1} = b + ac,$$

where a and b are constants for any particular salt at a given temperature.

Most of the previous investigations on the electrical conductivity of flames have been made in an ordinary Bunsen flame the temperature of which is about 2000° K. The methods used in the present experiments are similar to those used by B. T. Barnes (Phys. Rev., Feb. 1924) except that all his measurements were done on a flame at about 2000° K., while in the present experiments the temperature was varied from about 1500° K. to 2000° K.

Description of Apparatus.

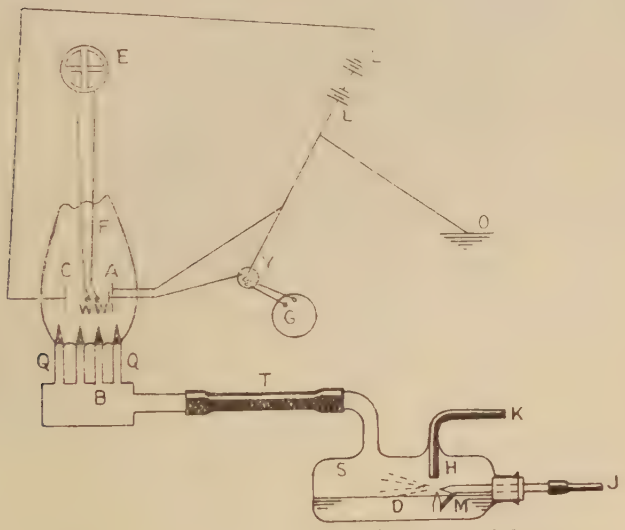
The Burner.—A special burner is used which gives a much steadier flame than other types of burners. It consists of four quartz tubes sealed with sealing-wax to a brass chamber. Fig. 1 shows the arrangement. A short piece of wide rubber tubing connects the burner to a specially constructed glass vessel, hereafter referred to as the sprayer.

The Sprayer.—It will be noticed from fig. 2 that this vessel, besides functioning as a sprayer, is the mixing chamber of air, coal-gas, and carbon dioxide, as well as the fine spray of the liquid being sprayed. Air supplied by an electric pump (P) enters the sprayer which contains a known volume of salt solution, distilled water, or some other liquid. The latter is sprayed in the manner shown in the diagrams. The reason that the rubber tube (H) is led well into the sprayer is to prevent improper mixing of the gas with the air and spray which would otherwise occur. The rubber tube (H) leads the coal-gas and CO_2 into the spray at its source.

The Coal-gas Regulator.—The gas before reaching the sprayer is passed through a regulator consisting of a

cylindrical jar (J) suspended from a balance with its open end downwards. This jar dips into a larger one (W_2) filled with water. An open vertical glass tube surrounded by one of larger diameter is clamped over a small vessel (V) of mercury which rests on the top of the jar (J). The gas enters through the outer tube, which dips well into the mercury, and escapes along the surface of the mercury into the inner tube. The gas is also led into the space within the jar (J). The arrangement is such that, when the gas

Fig. 1.



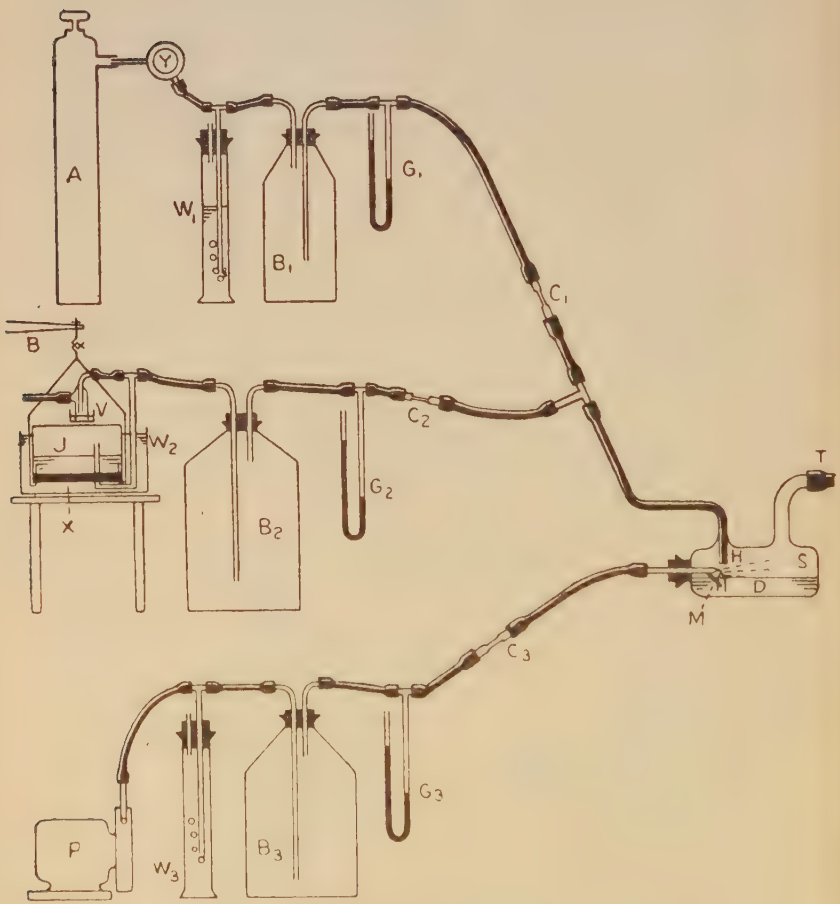
A. Anode.
B. Burner.
C. Cathode.
D. Solution sprayed.
E. Quadrant electrometer.
F. Flame.
G. Galvanometer.
H. Rubber tubing.
J. Air inlet.
K. Coal-gas inlet.
LL. Battery.
M. Solid glass connexion.
O. Earth.
QQ. Quartz tubes.
S. Sprayer.
T. Wide rubber tubing.
WW. Exploring wires.
Y. Ayrton shunt.

pressure increases, the jar (J) moves upwards, pressing the mercury up against the inner tube and thus allowing less gas to flow. Conversely, when the gas pressure decreases the jar (J) moves downwards allowing more gas to flow.

After leaving the regulator the gas passes through a large bottle (B_2), which smooths out small oscillations in pressure, and in order to increase the sensitiveness of the water

manometer (G_2), which indicates the pressure, the gas passes through a constriction (C_2) before entering the sprayer.

Fig. 2.



A. Cylinder of compressed CO_2.
B. Arm of balance.
B_1, B_2, B_3. Large bottles.
C_1, C_2, C_3. Constrictions.
D. Salt solution.
G_1, G_2. Water manometers.
G_3. Mercury manometer.
H. Rubber tubing.
J. Cylindrical jar.
M. Solid glass connexion.
P. Air-supply pump.
S. Sprayer.
T. Wide rubber tubing.
V. Vessel of mercury.
W_1, W_2. Jars of water.
W_3. Jar of mercury.
X. Heavy brass ring.
Y. Regulator.

The Air Supply.—Part of the air supplied by the pump (P) escapes by bubbling through mercury (W_3), thus securing constant pressure. The air supply is regulated by altering the current driving the pump. Any small variations in pressure are removed in the large bottle (B_3), and the pressure is measured by a mercury gauge (G_3) whose sensitiveness is increased by using a constriction (C_3).

The CO_2 Supply.—A cylinder (A) of compressed carbon dioxide is used to lower the temperature of the flame when required. After passing through a regulator (Y), the CO_2 partly escapes by bubbling through water (W_1) to secure constant pressure. Similarly to the coal-gas and the air, the CO_2 passes through a large bottle (B_1) and a constriction (C_1), the water-gauge (G_1) indicating the pressure.

The Flame.—The flame produced by burning the mixture of air, spray, coal-gas, and CO_2 from the quartz tubes (QQ) was very steady. On each quartz tube there was a well-defined inner cone. It is important that these cones should be free from any unsteadiness, and it was only after preliminary experiments with different burners and care in producing a perfect admixture of the gases that the cones refrained from jumping slightly.

The Electrodes.—Two platinum electrodes, made of thick foil, and welded to platinum wires about 1 mm. in thickness, are placed just above the cones in the flame (see fig. 1). The horizontal distance between the electrodes was $3\frac{1}{2}$ cm. The platinum wires are supported by covering them with quartz tubes having a small bore. In this way the platinum wires do not bend with the heat of the flame. Their ends are fused into glass tubes which are supported on stands, the platinum wires being sufficiently long to prevent the ends of the glass tubes getting very hot. The cathode (C) is 1 cm. square, and the anode (A) consists of a disk 4·5 mm. in diameter surrounded by a guard-ring 1 cm. square and inner diameter 5·5 mm. The disk is placed slightly in front of the guard-ring to keep the latter from shielding the disk from the heat of the flame.

Connexions.—The electrical connexions are shown in fig. 1. The current from a battery of small cells (LL) is passed between the electrodes. The quartz tubes (QQ) insulate the flame (F). The guarded disk is connected to a galvanometer (G) through an Ayrton shunt (Y); previous preliminary experiments showed that the lines of electric force between the electrodes are practically straight across for a small area, like that of the disk, in the middle of the electrodes. In this way the current passing through a known area of the flame is measured.

The Exploring Wires.—Two fine platinum exploring wires are placed 1 cm. apart in the flame, perpendicular to the direction of the lines of force between the electrodes. These wires are covered with quartz which allows only their tips to be exposed to the flame, the wires being fused to glass tubes supported on a stand. The wires can be moved about between the electrodes, and they are called exploring wires because when they are connected to a quadrant electrometer the potential gradient can be measured at any part of the electric field between the electrodes. The cathode is coated with lime in order to reduce the electrode drop of potentials a discovery made by Tufts in 1904. There is a region between the electrodes where the potential gradient is uniform, and it is in this region that the exploring wires (WW) are placed while measuring the conductivity of the flame. The quadrant electrometer and the battery of 120 volts for charging the needle are supported on a table with ebonite legs.

Measurement of the Temperature of the Flame.

To measure the temperature of the flame by means of a thermocouple is not very satisfactory because the thermocouple is at a lower temperature than the flame itself. The method used in the present experiments is that used by Barnes (*op. cit.*).

A strong solution of a sodium salt was put in the sprayer so that an intensely coloured sodium flame was obtained. White light from a gas-filled tungsten-filament incandescent lamp was passed through the flame, and its spectrum observed in a direct-vision spectroscope which separated the D lines very clearly. The temperature of the filament was adjusted so that the D lines were not visible on the continuous spectrum of the filament. If the filament was too hot the D lines were seen reversed as dark lines, and if too cold they were seen as bright lines. The temperature of the filament when adjusted is that when the D lines were not seen and was measured with an optical pyrometer supplied by the Cambridge Scientific Instrument Company.

The flame is by no means at a uniform temperature, the hottest part being found to be just above the cones. It is here that the electrodes are placed, and it is here that the temperature is measured. Different temperatures are obtained by altering the pressures of gas and CO_2, the air pressure being kept constant, since an alteration in the pressure of air would alter the concentration of salt in

the flame when salt solutions are being sprayed. The following table gives the pressures of air, coal-gas, and CO_2 for the different temperatures measured :—

Temperature (° absolute).	Air pressure (mm. of Hg).	Coal-gas pressure (mm. of H_2O).	CO_2 pressure (mm. of H_2O).
1920	90	17	0
1870	90	20	0
1720	90	20	20
1670	90	20	25
1570	90	17	33

These temperatures were measured when sodium-carbonate solution was being sprayed. It is of course assumed that the temperatures remain unaltered when other salt solutions are being sprayed so long as the conditions of spraying remain the same. The pressures of air, coal-gas, and CO_2 were very steady with the apparatus described above, and no difficulty at all was experienced in securing constant pressures.

Measurement of the Velocity of the Flame.

The special apparatus used for measuring the velocity of the flame is shown in fig. 3 and will now be described. A large wheel (W) having four openings (D D D D) round its circumference is mounted on the same shaft as that turning a stop-cock (S) which is open four times in each revolution of the shaft. An electric motor causes the shaft to rotate at about 2000 revolutions per minute ; the stop-cock is therefore opened and closed very rapidly.

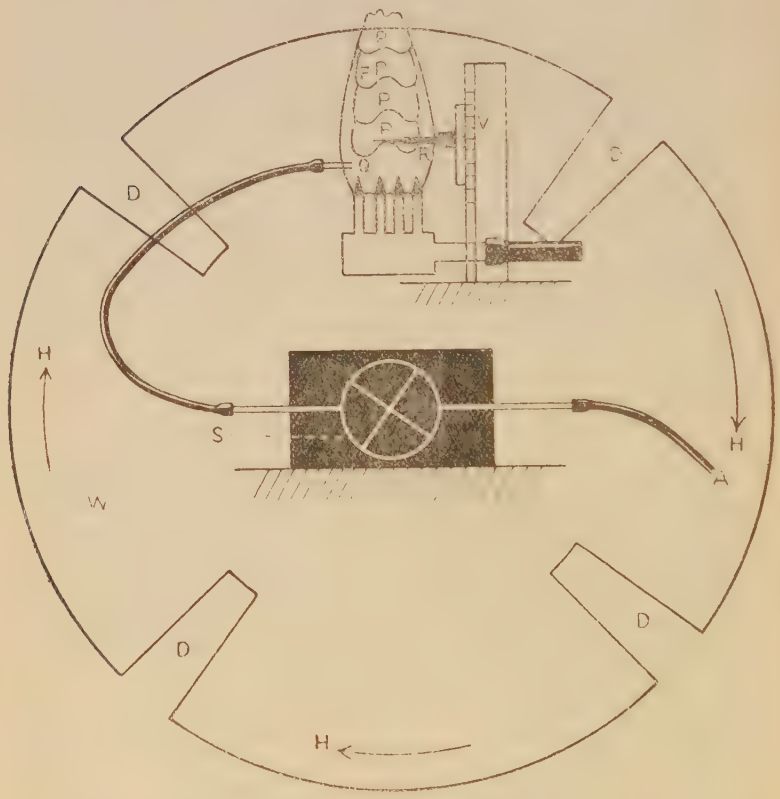
During this experiment distilled water is sprayed so that a non-luminous flame is obtained. A second sprayer containing a saturated solution of sodium chloride causes a mixture of air and vapourized salt (A) to pass through the stop-cock four times in each revolution of the shaft. Thereafter the mixture enters the flame through a narrow horizontal quartz tube (Q) placed at the bottom of the flame.

The wheel (W) rotates in the direction of the arrow-heads (H H H) with the same angular velocity as the stop-cock (S). The flame will therefore be seen as many times per second as the stop-cock is opened, when the flame is viewed through the stroboscopic wheel. By means of a pinch-cock the pressure of air and salt spray can be diminished till the puffs disappear, or increased until the puffs are very luminous.

The shape and position of the puffs can be seen from the diagram.

The flame is shielded from the draught of air caused by the rotation of the wheel by enclosing the latter in a wooden

Fig. 3.



A. Air and spray inlet.
B. Burner.
D, D, D, D. Openings on wheel.
F. Flame.
P, P, P, P. Puffs of sodium vapour.
Q. Narrow horizontal quartz tube.
R. Fine solid quartz tube.
S. Stop-cock.
V. Vernier and vertical sale.
W. Stroboscopic wheel.

box with glass windows. The distance between the puffs is measured by inserting a fine solid quartz rod in the flame supported on a vertical slide. The slide is provided with a millimetre scale and a vernier.

If v is the upward velocity of the flame in cm. per second, n the number of puffs per revolution of the shaft, r the number of revolutions of the shaft per minute, x the distance between successive puffs in cm., as seen through the stroboscopic wheel, then

$$v = nrx/60.$$

About four puffs could be seen in the flame, the distance between successive puffs being nearly the same. The velocity of the flame was measured in this way for each temperature given in the preceding section. The values given in the following table are mean values obtained from a number of readings.

Temperature of Flame (° K.).	Velocity of Flame (cm. per sec.).
1920	422
1870	419
1720	394
1670	387
1570	392

Amount of Salt in the Flame.

The amount of salt per c.c. in the flame depends on (1) the amount of solution sprayed per second; (2) the upward velocity of the flame; (3) the cross-section of the flame. In the previous section we have determined (2) for each temperature. With regard to (3), since the flame is rectangular just above the cones the cross-section can easily be measured. The following table gives the results obtained:—

Temperature (° K.).	Cross-section of Flame (sq. cm.).
1920	2·5×5·3=13·2
1870	2·6×5·4=14·0
1720	2·1×5·2=10·9
1670	2·0×5·2=10·4
1570	2·0×5·1=10·2

We have now to consider (1). Since the air pressure on the sprayer is kept constant throughout the experiment the volume of solution sprayed per second remains constant, no matter which solution is being sprayed. The method used for determining the volume of solution sprayed per second is the same as that of Barnes (*op. cit.*).

One hundred c.c. of sodium chloride solution, not necessarily of known strength, is put in the sprayer and sprayed for three hours under constant air pressure (viz. 90 mm. of Hg). The contents of the sprayer are then emptied into a beaker, and care is taken to see that no solution is left in the wide rubber tubing (T, fig. 1) and the burner. The latter are therefore washed out with distilled water, which is then emptied into the beaker.

One hundred c.c. of the sodium chloride solution is titrated with a solution of silver nitrate (not necessarily of known strength), and it is found that a volume V_1 of silver-nitrate solution is just sufficient to neutralize the sodium-chloride solution. If a volume V_2 of the same silver-nitrate solution is just sufficient to neutralize the contents of the sprayer, etc., in the beaker, after spraying, then the fraction of the salt sprayed $= 1 - \frac{V_2}{V_1}$.

It is quite wrong to weigh the sprayer and burner before and after spraying to obtain the amount of solution sprayed, because when the solution is sprayed for a long time considerable evaporation takes place. In the experiments to be described later, when solutions of different salts are sprayed, the quantity of solution placed in the sprayer is always 100 c.c., in order that the conditions of spraying should be the same as when the present experiment was performed.

The number of litres (V) of solution entering the flame per second is given by the equation:

$$V = \left(1 - \frac{V_2}{V_1}\right) \frac{100}{3600 \times 3 \times 1000}.$$

$\left(1 - \frac{V_2}{V_1}\right)$ was found to be ·1026.

We have now considered (1), (2), and (3), and are in a position to determine the amount of salt per c.c. in the flame. Let m denote the number of gram-molecules of metal vapour per c.c. in the flame, k the concentration of solution sprayed into the flame in gram-molecules per litre, G a constant for any particular temperature; then

$$m = Gk.$$

G is determined from the velocity (v) of the flame gases in cm. per sec., the cross-section (a) of the flame in square cm., and the number of litres (V) of solution entering the flame per second. Thus

$$G = V/av.$$

The following table gives the values of G calculated from this equation from the values of V, a, c already given :—

Temperature.	10^{10} G.
1920	1·71
1870	1·62
1720	2·21
1670	2·36
1570	2·37

Since G has now been determined, m is known for any concentration (k) of solution sprayed.

Specific Conductivity of the Flame.

If i amperes is the current measured by the galvanometer, X volts per cm. the potential gradient measured by the electrometer, A square cm. the area of the guarded electrode, the specific conductivity (s) is given by the equation :

$$s = \frac{i}{AX} \text{ amperes per sq. cm./volts per cm.}$$

The method of making an experiment to measure the specific conductivity of the flame will now be described. The burner and sprayer are removed and washed out with distilled water. They are then replaced and thoroughly dried by air supplied by the electric pump (P). One hundred c.c. of distilled water, measured by a pipette, are inserted in the sprayer. The coal-gas is then turned on and lighted. Air is supplied until the mercury pressure gauge registers 90 mm., and as the air pressure gradually increases the cones in the flame begin to appear and then grow smaller and smaller. The flame when distilled water is sprayed is a non-luminous one, very different from the flame when ordinary undistilled water is sprayed which contains salt in small quantities, colouring the flame. The electrodes become intensely luminous, the guarded disk of the anode being less bright than the rest of that electrode unless the guarded disk is placed slightly in front of the latter, as shown in fig. 1. This shows that the guard-ring had a tendency to shield the disk from the heat of the flame. When the pressures of coal-gas and CO_2 are adjusted to the various temperatures, readings of the galvanometer and quadrant galvanometer are taken. The flame is then extinguished.

The burner and sprayer are removed as before, washed out with distilled water, and thoroughly dried by air. One hundred c.c. of the solution to be sprayed are inserted in the sprayer and, as in the case when distilled water was sprayed, galvanometer and electrometer readings are taken at each temperature.

The measurement of the conductivity of the flame when distilled water is sprayed before each measurement of the conductivity of the flame when salt solutions are sprayed serves a double purpose. Its first use is as a gauge of the constancy of the apparatus. Secondly, to obtain the conductivity of the vapourized salt in the flame it is necessary first to obtain the conductivity of the flame without salt, but without altering the flame in any other way. The spraying of distilled water gives the flame the same vapour content as when salt solutions are sprayed.

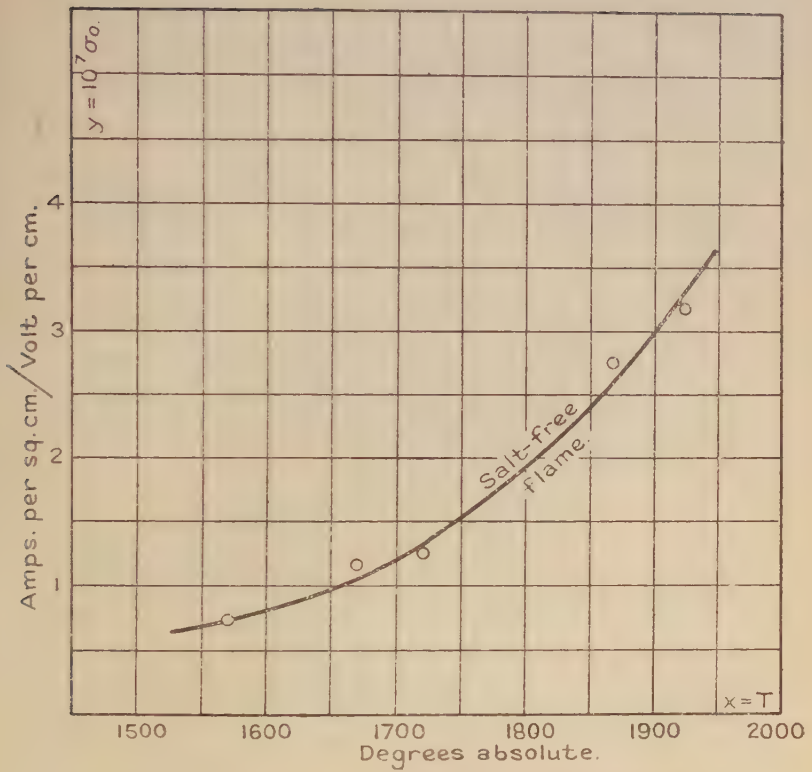
Variation of the Conductivity of the Flame without Salt with Temperature.

Since the conductivity (σ_0) of the flame without salt was measured before each experiment on the conductivity (σ) of the salted flame, a considerable number of values of σ_0 were obtained. The curve shown in fig. 4 is therefore an average one, and the values indicated on the diagram by small circle are the average of the total number obtained during the course of the experiments. They are given in the following table :—

T.	$10^7\ \sigma_0$.
1920	3·19
1870	2·74
1720	1·28
1670	1·13
1570	0·73

Throughout this paper the temperatures are expressed in degrees absolute and the conductivities in *amperes per square cm.* per *volts per cm.* It will be noticed that the conductivity of the flame increases with the temperature in accordance with the theory that the flame gases are ionized, electrons and positive ions being formed, and that there is equilibrium between these electrons and positive ions and those flame atoms which are not ionized.

Fig. 4.



Calculation of the Ionization Potential of Salt-free Flame from Temperature Variation.

Saha showed (Phil. Mag. vol. xl. p. 478 (1920)) that the thermal ionization of the neutral atoms (M) of gaseous elements into positive ions ($\overset{+}{\mathrm{M}}$) and electrons ($\overset{-}{\mathrm{E}}$) is a sort of chemical reaction satisfying the equation :

$$\mathrm{M} \rightleftarrows \overset{+}{\mathrm{M}} + \overset{-}{\mathrm{E}} - \mathrm{U},$$

where U is the quantity of energy absorbed in the process. The electron is assumed to be a monatomic gas of atomic weight 1·1836. The energy U can be expressed in terms of the ionization potential (V), which is the potential required to give an electron enough energy to ionize a neutral atom. If N is Avogadro's constant,

$$\mathrm{U} = (\mathrm{V}e\mathrm{N})/(\mathrm{J} \cdot 300) = 2{\cdot}302 \times 10^4\,\mathrm{V} \text{ calories.}$$

Since $2{\cdot}302\times10^4/4{\cdot}571 = 5048$, Saha's thermodynamic equation

$$\log_{10}\mathrm{K} = -\frac{\mathrm{U}}{4{\cdot}571\mathrm{T}} + 2{\cdot}5\log_{10}\mathrm{T} - 6{\cdot}56,$$

where K is the ionization equilibrium constant, becomes

$$\log_{10}\mathrm{K} = -\frac{5048\mathrm{V}}{\mathrm{T}} + 2{\cdot}5\log_{10}\mathrm{T} - 6{\cdot}56. \quad . \quad . \quad (1)$$

If K_{01} and K_{02} are two values of the ionization constant for the flame gases at temperatures T_1 and T_2 respectively,

$$\log_{10}(\mathrm{K}_{02}/\mathrm{K}_{01}) = 5048\mathrm{V}_0\left(\frac{1}{\mathrm{T}_1} - \frac{1}{\mathrm{T}_2}\right) + 2{\cdot}5\log_{10}\frac{\mathrm{T}_2}{\mathrm{T}_1}, \quad (2)$$

V_0 being the ionization potential for the salt-free flame.

Let $\bar{p}_0$ denote the partial pressure due to the electrons in the flame without salt, $\overset{+}{p}_0$ that due to the positive ions, and p_0 that due to the neutral atoms. If K_0 is the ionization constant for the salt-free flame,

$$\mathrm{K}_0 = \frac{\bar{p}_0\overset{+}{p}_0}{p_0} = \frac{(\bar{p}_0)^2}{p_0}, \text{ since } \bar{p}_0 = \overset{+}{p}_0.$$

$\bar{p}_0 = \overset{+}{p}_0$ because the number of electrons in the flame is equal to the number of positive ions, and the partial pressures are proportional to the number of ions present. The conductivity (σ_0) is proportional to the number of electrons present, the conductivity due to the positive ions being negligible because their mobilities are so small compared with those of the electrons. Therefore

$$\bar{p}_0 = \mathrm{A}\sigma_0,$$

where A is a constant inversely proportional to the velocity of the electrons,

for if the number of electrons is kept constant the conductivity would only increase by an increase in the velocity of the electrons. It is shown in Part III. that the velocity of the electrons is nearly independent of the temperature. A is therefore almost constant for different temperatures.

If $\bar{p}_0$ is small compared with p_0, we have

$$\mathrm{K}_0 \propto \sigma_0^2.$$

Equation (2) now becomes

$$2\log_{10}\frac{\sigma_{02}}{\sigma_{01}} = 5048\mathrm{V}_0\left(\frac{1}{\mathrm{T}_1} - \frac{1}{\mathrm{T}_2}\right) + 2{\cdot}5\log_{10}\frac{\mathrm{T}_2}{\mathrm{T}_1}. \quad . \quad (3)$$

Putting

$\mathrm{T}_1 = 1920$, $\mathrm{T}_2 = 1570$, $\sigma_{01} = 3{\cdot}19\times10^{-7}$, $\sigma_{02} = 0{\cdot}73\times10^{-7}$,

the value of V_0 obtained is found to be 1·8.

Using this value of V_0, K_0 can be calculated for different temperatures from equation (1). The following table gives the results obtained :—

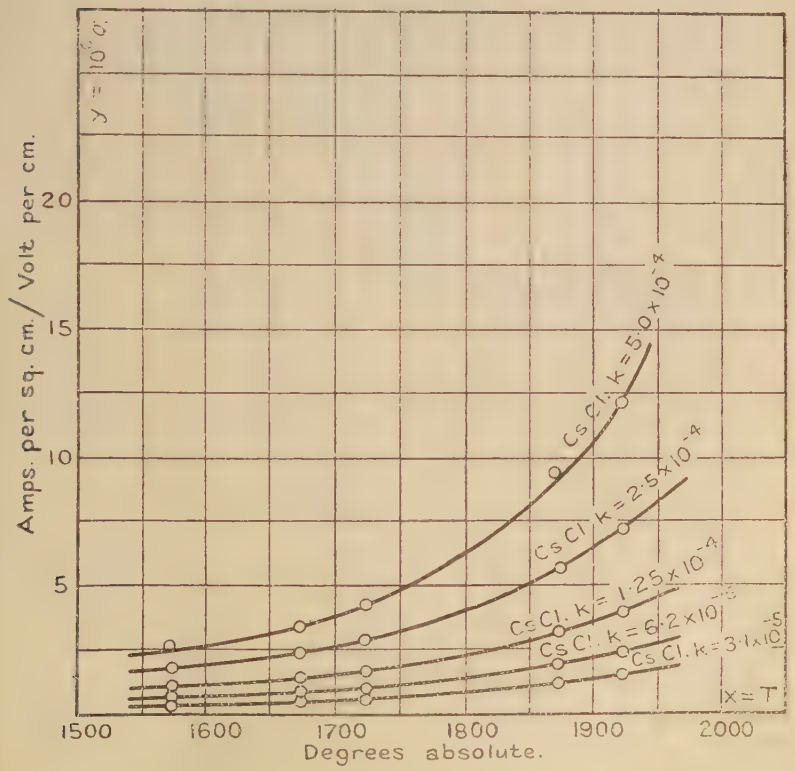
T.	$10^4 K_0$.	$10^{-4} K_0^{\frac{3}{2}}/\sigma_0$=const.
1920	7·95	8·8
1870	5·50	8·5
1720	1·62	9·9
1670	1·05	9·1
1570	0·40	8·6

Since the last column in the table is nearly constant, the value 1·8 for the ionization potential of the salt-free flame holds good for a temperature variation of 350 degrees.

Variation of the Conductivity of Cæsium Chloride and Rubidium Chloride with Temperature and Concentration.

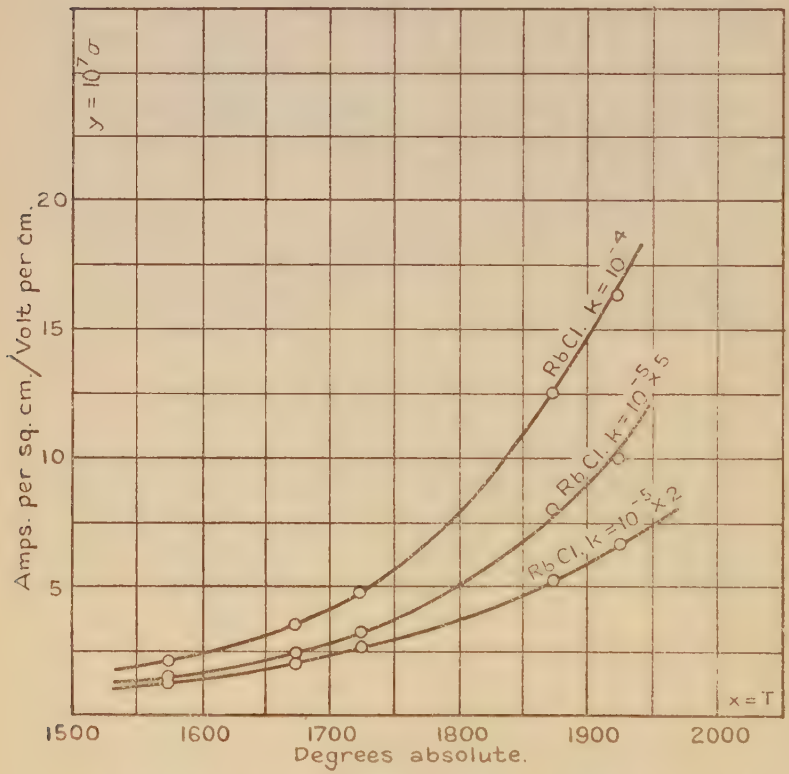
Figures 5 and 6 show the variation of the conductivity of the flame containing various salts in different concentrations

Fig. 5.



with the temperature. By comparing these curves with that for the salt-free flame (fig. 4) it will be noticed that the conductivity of the salt-free flame is several times less than the conductivity of a flame containing the spray of a very

Fig. 6.



dilute solution of salt. The following tables give the results obtained, k being the concentration of the solution sprayed in gram-molecules per litre :—

CsCl.

$10^6\,\sigma$.

T.	$k = 31\times10^{-4}$.	$k = 62\times10^{-4}$.	$k = 1{\cdot}25\times10^{-4}$.	$k = 2{\cdot}5\times10^{-4}$.	$k = 5{\cdot}0\times10^{-4}$.
1920 ...	1·45	2·37	3·81	7·13	12·1
1870 ...	1·35	1·83	3·13	5·61	9·3
1720 ...	0·69	1·11	1·69	2·91	4·22
1670 ...	0·58	0·87	1·32	2·39	3·40
1570 ...	0·46	0·76	1·03	1·75	2·55

RbCl.

T.	$10^7\sigma$. $k=2\times10^{-5}$.	$k=5\times10^{-5}$.	$k=10\times10^{-5}$.
1920	6·50	9·83	16·35
1870	5·28	8·10	12·60
1720	2·58	3·18	4·67
1670	2·00	2·45	3·40
1570	1·25	1·45	2·00

Part II.

The Thermal Ionization of Gaseous Elements at High Temperatures—A Confirmation of the Saha Theory.

H. A. Wilson's equation, viz.,

$$\frac{kc}{c^2-1} = b + ac,$$

is obtained in the following way, under the assumptions that both the salt and some constituent of the flame are ionized and that there is equilibrium between the electrons and positive ions formed and the neutral atoms (atoms not ionized). If K, K_0 are the ionization equilibrium constants for the salt and flame constituent respectively,

$$K = \overset{+}{p}\overset{-}{p}/p, \quad \ldots\ldots \quad (1)$$

$$K_0 = \overset{+}{p}_0\overset{-}{p}/p_0, \quad \ldots\ldots \quad (2)$$

$\overset{+}{p}$, $\overset{-}{p}$, p, $\overset{+}{p}_0$, p_0 being the partial pressures respectively due to the positive salt ions, the electrons, the neutral salt atoms, the positive flame ions, and the neutral flame atoms. As pointed out in a preceding section, the conductivity is proportional to the number of electrons present, and therefore, if c is the ratio of σ to σ_0, A a constant,

$$Ac = \overset{-}{p} = \overset{+}{p} + \overset{+}{p}_c, \quad \ldots\ldots \quad (3)$$

since the number of electrons is equal to the number of positive ions.

Assuming, as before, that $\overset{-}{p}$ is small compared with the total pressure, we have

$$p + \overset{+}{p} = m\mathrm{RT}, \quad \ldots\ldots \quad (4)$$

where R is the gas constant for one gram-molecule. From a preceding section we have

$$m = k\mathrm{G}. \quad \ldots\ldots \quad (5)$$

From (1) $$p=\overset{+}{p}\overset{-}{p}/\mathrm{K}\ ;$$

therefore (4) becomes

$$\overset{+}{p}=k\mathrm{GRT}\Big/\left(1+\frac{\overset{-}{p}}{\mathrm{K}}\right);$$

also, from (2),

$$\overset{+}{p}_0=p_0\mathrm{K}_0/\overset{-}{p}\ ;$$

substituting for $\overset{+}{p}$ and $\overset{+}{p}_0$ in (3), we get

$$\mathrm{A}c=k\mathrm{GRT}/(1+\mathrm{A}c/\mathrm{K})+p_0\mathrm{K}_0/\mathrm{A}c. \quad . \quad . \quad . \quad (6)$$

When $k=0$, $c=1$; therefore $p_0\mathrm{K}_0/\mathrm{A}=\mathrm{A}$.

Therefore (6) becomes

$$k\mathrm{GRT}/(\mathrm{A}c-\mathrm{A}/c)=1+\mathrm{A}c/\mathrm{K},$$

or $$kc/(c^2-1)=\mathrm{A}/\mathrm{GRT}+c\mathrm{A}^2/\mathrm{GRTK}.$$

Putting $$b=\mathrm{A}/\mathrm{GRT},\quad a=\mathrm{A}^2/\mathrm{GRTK},$$

$$kc/(c^2-1)=b+ac,$$

and $$\mathrm{K}=b^2\mathrm{GRT}/a. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Since a and b are constants for any one temperature, $kc/(c^2-1)$ is a linear function of c. The curve represented by Wilson's equation will therefore be a straight line, the ordinates and abscissæ being respectively $kc/(c^2-1)$ and c.

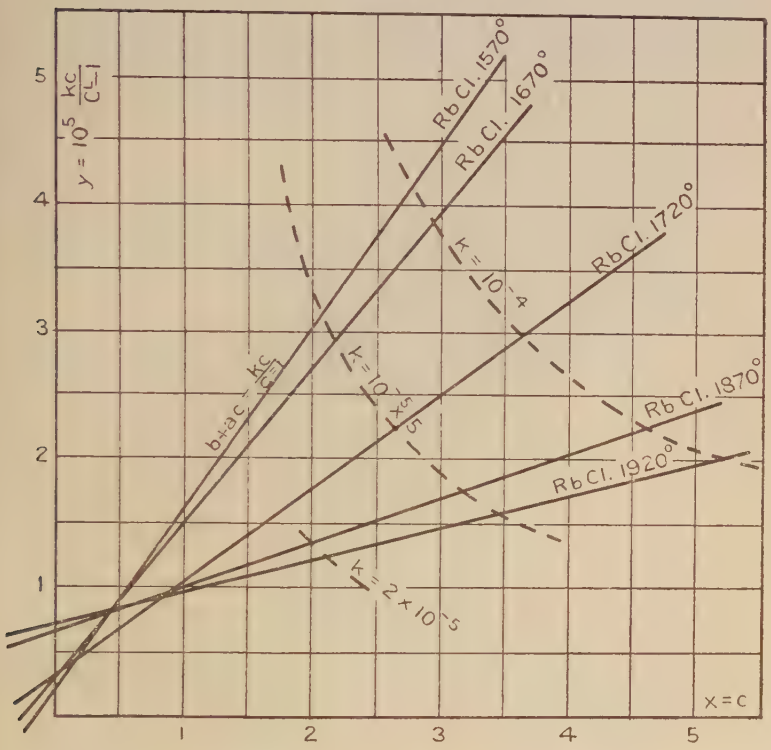
If the straight line be produced backwards to meet the $kc/(c^2-1)$ axis, b will be the ordinate at $c=0$. a will be the slope of the line. In order to obtain b accurately we must use small values of c, and therefore the solutions sprayed must be very dilute ; but if c is so very small that c^2-1 is very small, the error in $kc/(c^2-1)$ will be very great. Hence those values of c which are very small are of little use to calculate b accurately.

The results which were obtained with rubidium chloride were considered the best for calculating b. H. A. Wilson showed in 1915 (*op. cit.*) that b is proportional to the molecular weight of the salt. For this reason the b's of NaCl, KCl, and LiCl are too small to be calculated with any degree of accuracy.

Fig. 7 shows the straight lines represented by Wilson's equation obtained from the results of rubidium chloride at different temperatures. In order that the b's should be obtained as accurately as possible small enough values of c

must be used. The curves for cæsium chloride (see fig. 5) do not give small enough values of c.

Fig. 7.



The following table gives details of the calculations, the last column being the values of $\log_{10} K$ calculated from Saha's theory on the assumption that the ionization potential of rubidium is 4·154; the second last column gives the values derived from the flame conductivities :—

T.	$10^{10}G$.	$10^7\sigma_0$.	$10^5 b$.	$10^5 a$.	$10^5 \frac{b^2}{a}$.	$\log_{10}\left(\frac{b^2}{a}\right)$.	$\log_{10}(GRT)$.	$\log_{10}K$. Observed.	$\log_{10}K$. Theoretical.
1920...	1·71	3·17	·71	·25	2·02	$\bar{5}$·305	$\bar{5}$·436	− 9·26	− 9·26
1870...	1·62	2·74	·65	·34	1·24	$\bar{5}$·093	$\bar{5}$·401	− 9·51	− 9·58
1720...	2·21	1·285	·32	·72	0·142	$\bar{6}$·152	$\bar{5}$·500	−10·35	−10·68
1670...	2·36	1·122	·26	1·24	0·054	$\bar{7}$·736	$\bar{5}$·515	−10·76	−11·05
1570...	2·37	0·73	·18	1·45	0·022	$\bar{7}$·352	$\bar{5}$·491	−11·16	−11·94

It will be noticed that the ionization constants derived from the flame conductivities are of the same general magnitude as those derived from Saha's thermodynamic equation at the highest temperatures, but there is considerable disparity at the lower temperatures. The results, therefore, show that Saha's theory holds good only at high temperatures.

Part III.

Velocity of Electrons in a Bunsen Flame.

From the results of the experiments described in this paper, the velocity of the electrons in the flame can be calculated in the following way :—

If n is the number of electrons per c.c., u the velocity of an electron due to an electric field of one volt per cm., then

$$\sigma_0 = une.$$

If N is Avogadro's constant,

$$p = n\mathrm{RT}/\mathrm{N}.$$

Then, since $\mathrm{N}e = 96500$,

$$u = \sigma_0/(b\mathrm{G} \times 96500).$$

The following table gives the results calculated from the foregoing experiments :—

T.	$\sigma_0 \times 10^7$.	$b \times 10^6$.	$\mathrm{G} \times 10^{19}$.	u (cm., sec.).
1920	3·17	·73	1·71	2700
1870	2·74	·65	1·62	2700
1720	1·285	·32	2·21	1900
1670	1·122	·26	2·36	1900
1570	0·73	·18	2·37	1800

In conclusion the writer wishes to say that the subject was suggested to him by Professor H. A. Wilson, F.R.S., under whose guidance the research was begun. The writer desires to thank Professor H. A. Wilson and Professor E. Taylor Jones for supervising his work, and the University of Glasgow for facilities for research in the Natural Philosophy Research Laboratory.

XIII. *Merton's Method of Measuring the Half-Width of a Spectral Source. By* JOHN K. ROBERTSON, *Queen's University, Kingston, Canada* *.

1. THE pioneer work of Rayleigh and Schönrock has shown that, in the case of a gas at low pressure, it is possible to evaluate the mass of a radiating particle by making use of the expression :

$$\frac{\delta\lambda}{\lambda} = 3{\cdot}57 \times 10^{-7} \sqrt{\frac{\mathrm{T}}{m}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

T = absolute temperature of the radiating gas,

m = the mass of an individual radiator in terms of the hydrogen atom as unit,

$\delta\lambda$ = the half-width of the spectral source as defined in 2 below.

Experimentally, therefore, the evaluation of m consists essentially in the determination of $\delta\lambda$. This can be done in two ways: (1) by observation of the maximum path difference for which interference can be obtained ; (2) by obtaining (with a high-power interference spectroscope) two photographs of a spectral line under conditions which permit of a known intensity change. Much use has been made of the first method by Fabry and Buisson and others, with results which are substantially in accord with theory. As far as the writer can gather, the second method has been used only by Merton †, to whom it is due. It has the distinct advantage over the first that the magnitude of m can be obtained without the adoption of any arbitrary value for the limiting visibility of fringes. In the case of hydrogen and helium, Merton obtained results which established the value of his method but which, in some cases, were not in as perfect agreement with Rayleigh's theory as might be wished. Moreover, his application of the method to the Echelon grating was based on the use of an intensity expression which is not rigorously true. It seemed desirable, therefore, to see if a more exact analytical development would reveal any sources of error other than those of an experimental nature. In the present paper this has been done, and results have been obtained which indicate to what extent Merton's simpler theory is justifiable.

* Communicated by the Author.

† Merton, Proc. Roy. Soc. A, xcvii. p. 307 (1920). Phil. Trans. Roy. Soc. A, ccxxii. p. 368 (1922).

2. If we assume that the lack of monochromatism in a spectral source is due chiefly to molecular or atomic motions, then the distribution of light emitted by a source is given by the exponential law,

$$E = E_0 e^{-k^2x^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where x is defined by the equation

$$\frac{1}{\lambda} = \frac{1}{\lambda_0}(1 \pm x), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

E = intensity corresponding to a wave-length λ differing in practice by a small amount from the central wave-length λ_0,

k^2 = a quantity whose magnitude is greater, the more nearly absolutely monochromatic light is approached.

In passing, we may note that in Rayleigh's theory k^2 is represented by $c^2\beta$ *.

Now, following Rayleigh and Michelson, we define the half-width of the source as given by the value of x for which $E = 0{\cdot}5\, E_0$. It follows from (2) and (3) that

$$\left(\frac{\delta\lambda}{\lambda}\right)^2 = \frac{\log_e 2}{k^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Experimentally, therefore, the determination of $\delta\lambda$ (and m) depends essentially on evaluating k^2.

3. Merton's method is based on the following considerations. The distribution of intensity in a spectral image, as formed by a high-power instrument, such as an echelon grating, is given by the law

$$I = I_0 f(\phi, k^2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

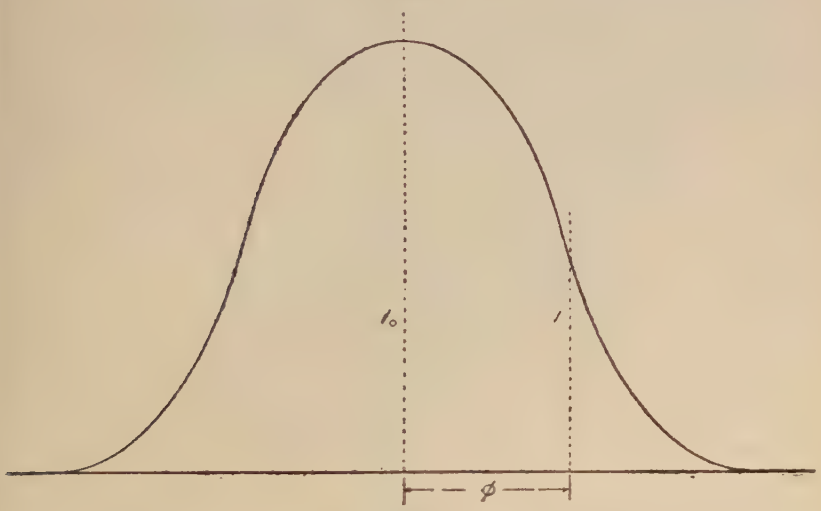
where ϕ = angular distance from the centre,
I_0 = intensity when $\phi = 0$ (*vide* fig. 1).

It is important to distinguish clearly between equations (2) and (5). Fig. 1 and equation (5) have reference to a distribution of intensity in an actual image which is the result of two causes: (1) the conditions imposed on the light by the instrument; (2) the lack of monochromatism of the source. For example, in the echelon, *even with absolutely monochromatic light* ($k^2 = \infty$) there is a distribution similar to fig. 1 which, for low orders of interference, differs little from the resultant when lack of monochromatism is taken into consideration.

* Rayleigh, Phil. Mag. [6] xxix. p. 279 (1915).

Now, when photographing such an image, there is always a critical intensity which, in any given time, just produces a visible blackening on the plate. This, of course, corresponds

Fig. 1.



to the edges of the image. If I_c be such a critical intensity and ϕ_c the corresponding value of ϕ,

$$I_c = I_0 f(\phi_c, k^2). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Suppose, now, that two photographs are taken under such conditions that I_0 is changed by a known ratio from I_0' to I_0''—for example, by using, as Merton did, the single and double order images of an echelon.

Then

$$I_c = I_0' f(\phi_c', k^2),$$
$$I_c = I_0'' f(\phi_c'', k^2),$$

from which

$$I_0' f(\phi_c', k^2) = I_0'' f(\phi_c'', k^2). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From this relation, which is the basis of Merton's method, it is theoretically possible to calculate k^2. Before it can be used, it is obvious that the form of the function must be known.

4. In applying this method to the case of the single and double order images produced by an echelon, it is necessary to recall that we are dealing with diffraction through N slits

and that in consequence, *for monochromatic light*, the intensity in any direction θ is given by the relation :—

$$I_\theta = A_0^2 \cdot \frac{\sin^2\left(\frac{\pi R \sin\theta}{\lambda}\right)}{\left(\frac{\pi R \sin\theta}{\lambda}\right)^2} \cdot \frac{\sin^2\frac{N\delta}{2}}{\sin^2\frac{\delta}{2}}, \quad . \quad . \quad . \quad . \quad (8)$$

where

A_0^2 = intensity due to a single slit in direction $\theta = 0$,

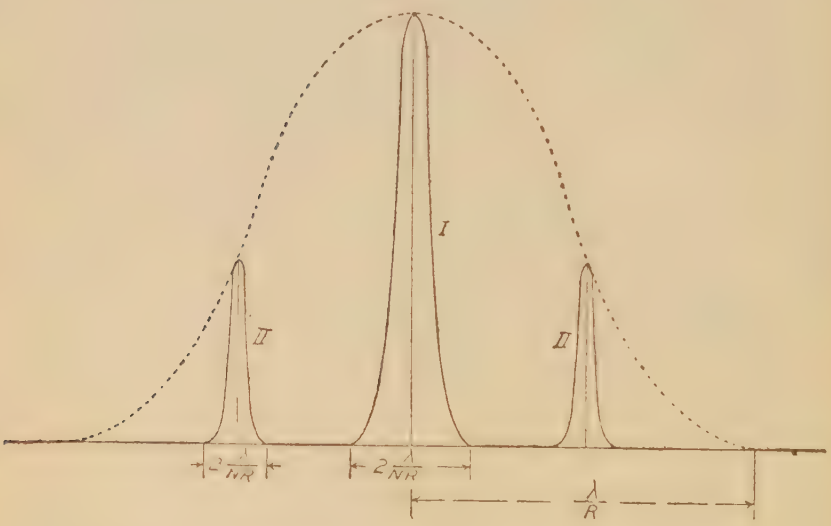
R = width of a single slit,

δ = the phase difference between the resultants of two successive slits,

$$= \frac{2\pi}{\lambda}\{(\mu-1)t + R\theta\},$$

t = thickness of an echelon plate.

Fig. 2.



The first factor gives the usual intensity distribution for a single slit, as represented by the dotted line in fig. 2. From the second factor we deduce the following.

(*a*) The existence of principal maxima (orders) when $\delta = p \cdot 2\pi$, that is, when

$$(\mu-1)t + R\theta = p\lambda,$$

where p, the order of interference, is an integer of magnitude of the order of 10^4 for $t = 1{\cdot}5$ cm. Moreover

since the maxima are $\frac{\lambda}{R}$ apart, we may have the echelon placed in either the single order position I (fig. 2), or the double order II (fig. 2).

(*b*) The intensity of such maxima falls to zero when θ is increased by $\frac{\lambda}{NR}$.

The actual distribution of light in one of these principal maxima is given, therefore, by

$$I_\phi = A_0^2 . \frac{\sin^2 \alpha}{\alpha^2} . \frac{\sin^2\left(\frac{N\pi R\phi}{\lambda}\right)}{\sin^2\left(\frac{\pi R\phi}{\lambda}\right)}, \quad . \quad . \quad . \quad . \quad (9)$$

where $\alpha = \frac{\pi R \sin\theta}{\lambda}$ and, for double order images, has values ranging from $\left(\frac{\pi}{2} + \frac{\lambda}{NR}\right)$ to $\left(\frac{\pi}{2} - \frac{\lambda}{NR}\right)$; for single order, from $+\frac{\lambda}{NR}$ to $-\frac{\lambda}{NR}$. In this relation ϕ represents the angular distance from the centre of an order, and has a maximum value of $\frac{\lambda}{NR}$.

5. Before Merton's method can be applied (equation 7), it is necessary to find how equation (8) is altered when we pass from monochromatic light to a source in which lack of monochromatism is defined by

$$E = E_0 e^{-k^2x^2}.$$

In the case of a Fabry and Perot interferometer this has been done by Saha *, while more generally the problem has been discussed by Gilchrist †. For the echelon the writer gives the following solution :—

If ΔI_ϕ = intensity, in direction ϕ from centre of an order, contributed by wave-lengths between x and $x + dx$, then

$$\Delta I_\phi = A_0^2 \frac{\sin^2 \alpha}{\alpha^2} . \frac{\sin^2 \frac{N\delta}{2}}{\sin^2 \frac{\delta}{2}} . e^{-k^2x^2} dx.$$

Hence

$$I_\phi = A_0^2 \int_{-\infty}^{+\infty} \frac{\sin^2 \alpha}{\alpha^2} . \frac{\sin^2 \frac{N\delta}{2}}{\sin^2 \frac{\delta}{2}} . e^{-k^2x^2} dx.$$

* Saha, Phys. Review, x. p. 782 (1917).
† Gilchrist, Phys. Review, xxvii. p. 596 (1926).

Now, it may be proved without difficulty that for large values of k^2 (such as is always the case in any problems dealing with half-width of spectral sources) the variation in the first factor due to lack of monochromatism may be neglected. We may write, therefore,

$$I_\phi = A_0^2 \frac{\sin^2 \alpha}{\alpha^2} \int_{-\infty}^{\infty} e^{-k^2x^2} \frac{\sin^2 \frac{N\delta}{2}}{\sin^2 \frac{\delta}{2}} . dx.$$

Now, since

$$\frac{\sin^2 \frac{N\delta}{2}}{\sin^2 \frac{\delta}{2}} = N + 2\{(N-1)\cos\delta + (N-2)\cos 2\delta + \ldots + \cos(N-1)\delta\}$$

and

$$\delta = \frac{2\pi}{\lambda}\{(\mu-1)t + R\theta\}$$
$$= 2\pi p(1 \pm x),$$

where p = order of interference for central wave-length λ_0, the above integral may be reduced to standard integrals of the types :

$$\int_{-\infty}^{+\infty} e^{-k^2x^2} dx \quad \text{and} \quad \int_{-\infty}^{+\infty} e^{-k^2x^2} \cos 2rx\, dx.$$

We have, therefore, as a final solution :

$$I = A_0^2 \frac{\sin^2 \alpha}{\alpha^2} \cdot \frac{\sqrt{\pi}}{k}\left\{N + 2(N-1)\cos l \,.\, e^{-\frac{l^2}{4k^2}} + \ldots + 2\cos(N-1)\, l \,.\, e^{-\frac{(N-1)^2 . l^2}{4k^2}}\right\}.$$

where $l = 2\pi p$. . . . (10)

6. This, then, is the rigorous form of the equation necessary for the use of Merton's method. In discussing the possibility of making practical use of it we may distinguish three cases :—

(*a*) When l^2 is so much *less* than $4k^2$ that all the exponential terms may be put equal to 1.

This is true to a high order of accuracy if

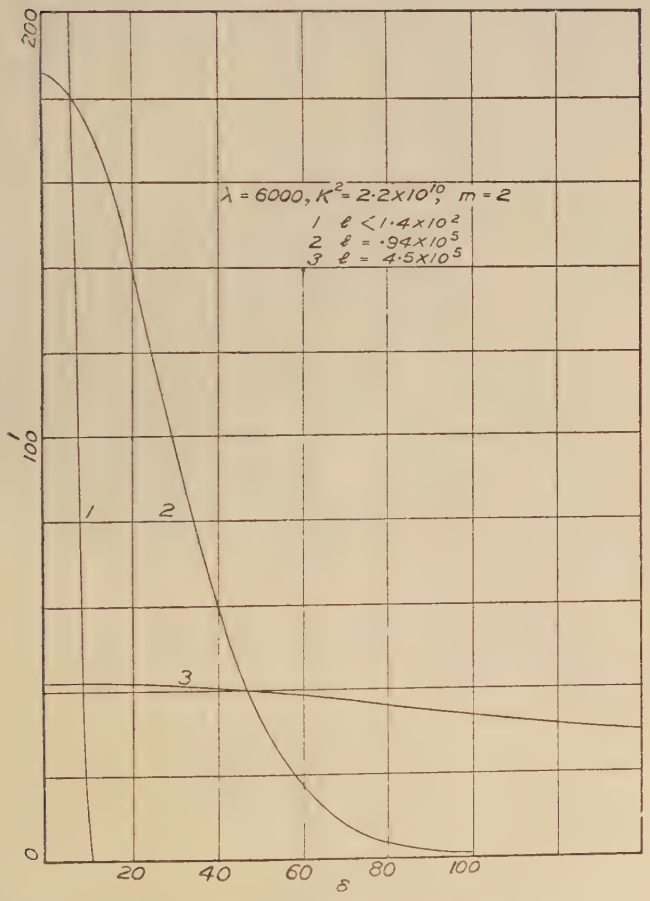
$$\frac{(N-1)^2 . l^2}{4k^2} < 10^{-2},$$

or, since k^2 for the hydrogen molecule from Rayleigh's theory $= 2{\cdot}25 \times 10^{10}$, if

$$l < \frac{3 \times 10^4}{N-1}.$$

In this case equation (10) reduces to equation (8), or, in other words, for a 35-plate echelon, if the order of interference is less than approximately $\frac{1}{2\pi} \cdot \frac{3 \times 10^4}{35}$, the distribution of intensity in the image differs from that for

Fig. 3.



ideally monochromatic light by less than a measurable amount. For low orders of interference, therefore, as Merton points out, his method cannot be used.

In fig. 3, graph 1 represents the variation in intensity for N=35, due to the second factor of equation (9) and hence also for equation (10), when p is small. In order to use a

convenient scale for the other graphs, only a portion of the curve is shown. The reader will understand that when $l=0$, or a multiple of 2π, the intensity is proportional to N^2, and therefore on the scale used in the graph is represented by 35^2 or 1225.

(*b*) When l^2 is so much *greater* than $4k^2$ that all but the first exponential term may be dropped.

This is so to less than 1·10 per cent. if $\frac{l^2}{4k^2}=2$; that is for $k^2=2{\cdot}25\times10^{10}$, if $l>4{\cdot}2\times10^5$.

In this case we may write

$$I = A_0^2\frac{\sin^2\alpha}{\alpha^2}\cdot\frac{\sqrt{\pi}}{k}\left\{N+2(N-1)\cos l\,.\,e^{-\frac{l^2}{4k^2}}\right\} \quad . \quad (11)$$

For equation (11), fig. 3, graph 3, represents the change in intensity due to the second factor. It will be noted that the visibility is so low that Merton's method is again not applicable.

(*c*) When l lies between the limits given in (*a*) and (*b*).

As a concrete example, we may take a value for l of the same order as that used by Merton. For $N=35$, $\lambda=6000$ Å., $t=1{\cdot}5$ cm., $\mu=1{\cdot}6$, $l=0{\cdot}94\times10^5$. Using this value of l, and again plotting the second term of equation (10), we obtain graph 2 of fig. 3. For such orders of interference, Merton's method is possible. Its actual application, however, by the use of equations (7) and (10) obviously would not be an easy matter. The necessity of retaining many of the exponential terms would render such a solution largely a matter of trial and extremely laborious.

7. It is important, therefore, to examine the simple expression with which Merton replaces equation (10). This he does by writing

$$I = A_0^2\frac{\sin^2\alpha}{\alpha^2}\cdot e^{-k\beta^2}. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

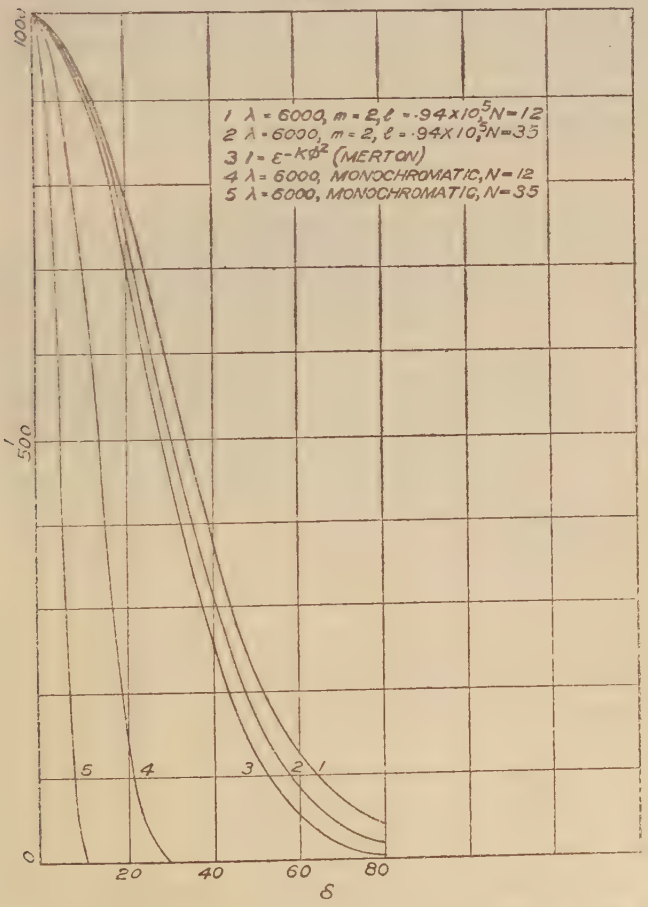
In considering to what extent equation (12) may be used as a substitute for equation (10), it is necessary to note one or two facts.

(*a*) Merton made the assumption that an exponential distribution in the source gives rise to an exponential distribution in the image, except for the alteration brought about by the superposition of the intensity pattern of a single slit. Now this cannot be accepted without some justification. In the first place, it neglects the finite width of the image which is caused by the instrument *even for monochromatic light*. Moreover, the assumption is tacitly

made that the intensity distribution is independent of the number of plates of the echelon.

To gain some idea of the error introduced by these factors, the curves of fig. 4 have been plotted. They all refer to the intensity distribution of a hypothetical H_2 wave-length

Fig. 4.



6000 Å., for an echelon with plates of thickness 1·5 cm., and index 1·6. Graph 1 is a plot of the second factor of equation (10) for a 12-plate instrument; graph 2 for one with 35 plates. Graph 3 is a plot of Merton's expression $e^{-k\phi^2}$, where k has been determined by the method indicated below; while graphs 4 and 5 represent the distribution for

absolutely monochromatic light, 4 for a 12-plate echelon, 5 for a 35-plate. For all the graphs, maximum intensity has been taken equal to 1000. While the departure of graph 3 from that given by the more accurate expression of equation (10) is not great for a 35-plate instrument, it is evident that even in this case an appreciable error may be introduced by Merton's assumption.

(*b*) The k in $e^{-k\phi^2}$ must not be confused with the k in e^{-k2x^2}. As already noted, in the latter expression k is a measure of the half-width *of the source*. Merton's k is defined in terms of the half-width *of the image*, and has a magnitude given by

$$k = \frac{\log_e 2}{(\delta\alpha)^2}, \quad \ldots\ldots \quad (13)$$

where $\delta\alpha$ is the value of ϕ for which $e^{-k\phi^2}$ has fallen 50 per cent. It has a different value, therefore, for each wave-length emitted by the same source, and cannot be used in equation (4) for the evaluation of $\delta\lambda$, the half-width of the source.

In Merton's method $\delta\lambda$ is obtained (1) by evaluating $\delta\alpha$ from observed data on spectrograms, (2) by assuming that the $\Delta\lambda$ which corresponds to $\delta\alpha$ in ordinary echelon theory correctly defines the half-width of the source as given by equation (1). As details of Merton's measurements were not available, a test of the validity of his method was made in the following way.

From the above definition of $\delta\alpha$,

$$\delta\lambda = \frac{\delta\alpha}{2\pi} \cdot \frac{\lambda^2}{bt}, \quad \ldots\ldots \quad (14)$$

since $\frac{\lambda^2}{bt}$ is the change in wave-length corresponding to a shift from one order to the next—that is, to a change in phase $= 2\pi$.

From (14) we have at once

$$\frac{\delta\lambda}{\lambda} = \frac{\delta\alpha}{2\pi} \cdot \frac{\lambda}{bt}. \quad \ldots\ldots \quad (15)$$

Hence, assuming the correctness of Rayleigh's theory as given by equation (1) for the hydrogen molecule, at T=456, we have

$$\cdot 53 \times 10^{-5} = \frac{\delta\alpha}{2\pi}\frac{\lambda}{bt}. \quad \ldots\ldots \quad (16)$$

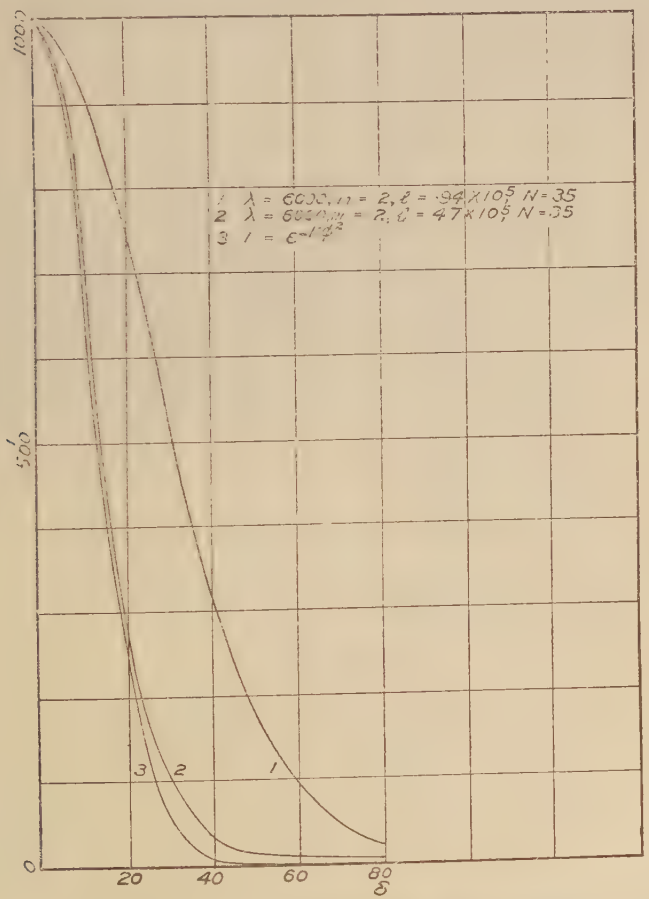
Taking $\lambda = 6000$ Å., $t = 1{\cdot}5$ cm., $b = {\cdot}6$ (a value, correct to

less than 1 per cent., for $\mu - 1 - \lambda \frac{\partial \mu}{\partial \lambda}$), we obtain

$$\delta\alpha = 28^{\circ}{\cdot}8.$$

From fig. 4, graph 2, the value of δ for which the intensity has fallen 50 per cent. is 31°, while graph 1 (the 12-plate echelon) gives 33°·5 *.

Fig. 5.



An additional test is provided by the graphs of fig. 5, where 1 is a repetition of 1 of fig. 4, while 2 illustrates the intensity distribution due to the second factor of equation

* To obtain values of k necessary for plotting $e^{-k\phi^2}$ as has been done in graph 3 of fig. 4 and graph 3 of fig. 5, $\delta\alpha$ was first of all found from equation (16) and then k from equation (13).

(10), for $\lambda = 6000$, $\mu = 1{\cdot}6$, but for a 35-plate echelon whose plates are of one-half the thickness of those corresponding to 1.

From (15) it follows at once that if $\delta\alpha_1$ and $\delta\alpha_2$ are values corresponding to t_1 and t_2,

$$\frac{\delta\alpha_1}{\delta\alpha_2} = \frac{t_2}{t_1}$$
$$= 2{\cdot}0 \text{ for the case assumed.}$$

Now from graphs 1 and 2 we obtain

$$\frac{\delta\alpha_1}{\delta\alpha_2} = \frac{31}{16} = 1{\cdot}9.$$

It is evident, therefore, that there is much to be said for the use of Merton's expression. At the same time there is sufficient evidence of possible errors introduced by the less rigorous method to justify a more careful test of the extent to which it may be used than has been possible in this paper.

The writer's thanks are due to Mr. John Findlay, B.A., who computed the numerical data from which the graphs of figs. 3, 4 and 5 were plotted.

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XIV. *Ionic Refractivity and the Scattering of Light by Gases.* *By* Prof. T. H. Havelock, *F.R.S.**

Introduction.

1. In most of the recent work on ionic refractivities it is assumed that molecular refractivity is additive. There is theoretical justification for this assumption when the substance is crystalline and of cubic type, though it appears to be only approximately true even in those cases. For the molecules of a gas it is clearly necessary to take into account the mutual action of the atoms or ions within each molecule.

A well-known approximation on the classical electromagnetic theory of dispersion consists in taking the atoms or ions in each molecule to be equivalent to isotropic

* Communicated by the Author.

resonators at fixed distances apart. This gives in general an anisotropic molecule, and so enables us to use another experimental fact, giving an additional equation between the various unknown quantities; this occurs when we know the ratio of the two components of light scattered by the gas in a direction at right angles to the incident beam.

The general dispersion formula contains a certain number of constants, two for each resonator together with the distances between their centres. In theory one might obtain these constants directly from the known dispersion of the gas, but in practice this is usually quite impracticable; the formulæ become rather complicated when there are more than two units, and also the dispersion is not usually known over a sufficient range of wave-length. So far the direct method has proved feasible only in one case, namely hydrogen, for which I gave the calculations a few years ago *. In that case the two units in the molecule are equal, and the dispersion formula involves only three constants; further, the dispersion is known accurately over the range 5462 to 1854 A.U. It was shown that the dispersion could be expressed very closely by a formula of the required type, and further that the values of the constants gave a value of the scattering ratio in agreement with experiment. The distance between the centres of the two units in the hydrogen molecule can also be deduced from the constants, and it is 1·39 Å.

In most of the gases we shall consider, the dispersion is known only over the range 6708 to 4800 Å.; and as it can be expressed quite well in this range by a simple two-constant formula, it is useless to attempt the direct determination of the constants of any more elaborate formula. We shall therefore use the formulæ not directly as dispersion formulæ, but as expressions for the refractivities of the constituent units at some standard wave-length.

This method has been used in recent papers by Ramanathan †, but more for calculating the interatomic distances in the molecule. For the molecule of an element, such as H_2, O_2, or N_2, there are only two unknown quantities: the refractivity of either unit of the molecule, and the distance between the two units; hence they can both be calculated from a knowledge of the refractivity of the gas and the ratio of the components in scattered light. In compound gases, such as CO_2, Ramanathan assumes the refractivity of the

* Proc. Roy. Soc. A, ci. p. 154 (1922).

† K. R. Ramanathan, Proc. Roy. Soc. A, cvii. p. 684 (1925); also *ibid.* A, cx. p. 123 (1926).

oxygen to be the same as in O_2; this seems inadmissible in general.

In the following paper we utilize in some cases estimates of molecular size and structure which have been made on other grounds; for example, from the theory of infra-red band spectra. The gases which are examined are first the series of hydrides HCl, HBr, H_2S, H_2O and some other triatomic gases such as N_2O, CO_2, and CS_2; molecules with four or five atoms are left for future consideration.

Dispersion of some Hydrides.

2. For the experimental values of the dispersion of the various gases, we shall use throughout the results given by the Cuthbertsons; an interesting point, which does not seem to have been noticed previously, arises from an inspection of their formulæ. Consider, for example, the case of HCl. On the older view the Hydrogen and Chlorine were supposed to be in the same state as in the respective molecules of those gases; but it proved to be quite impossible to make up the refractivity and dispersion of HCl out of those of $\frac{1}{2}H_2$ and $\frac{1}{2}Cl_2$. On the current view the units of HCl are supposed to be H^+ and Cl^-, the electron of the hydrogen atom having taken its place in the chlorine atom to complete the argon structure of the latter. On this view it is natural to assume the contribution of the hydrogen nucleus to the optical refractivity to be practically zero, apart possibly from a slight deformation of the outer shell of the chlorine ion due to the presence of the hydrogen nucleus within or near its effective boundary. Similar remarks apply to H_2S, PH_3, and so on in relation to argon, and the corresponding series HF, H_2O, NH_3, and so on in relation to neon.

Turn now to the experimental results, and instead of considering only refractivity, examine the dispersion of the gases. Cuthbertson * expressed his results in each case by a simple formula,

$$n^2-1 \doteqdot 2(n-1) = \frac{C}{p_0^2-p^2}, \quad . \quad . \quad . \quad . \quad (1)$$

n being refractive index and p frequency. This formula can be obtained by treating each molecule as a single isotropic resonator of natural frequency p_0; the constant C is proportional to the number of resonators per unit volume, and on the ordinary theory involves the effective dispersion charge

* Collected results given by C. Cuthbertson, Phil. Mag. xxv. p. 594 (1913).

and mass. Now, instead of thinking of the results in terms of elements and compounds, let us arrange the hydrides in series, each headed by the corresponding inert gas, and we get the following table for the constants C and p_0 :—

Gas.	$C\times10^{-27}$.	$p_0^2\times10^{-27}$.
Neon	5·1865	38196
HF	←	—
H_2O	5·2540	10697
NH_3	5·9316	8135
Argon	9·4326	17009
HCl	9·2850	10664
H_2S	9·668	7808
Krypton ...	10·6892	12768
HBr	10·2892	8668
Xenon	12·2418	8978
HI	11·58	6556

In this form the data are very interesting and suggestive ; they bear out clearly the modern view of the molecular structure of these substances. The small contribution of the hydrogen nucleus to the refractivity is indicated ; further, one might almost suggest that, if allowance could be made for this, then the value of C would be constant in any one set. Take, for example, the first set. The fluorine, oxygen, and nitrogen are in the form F^-, O^{--}, N^{---} respectively, and have the neon structure ; further, it seems that if we could express the refraction of each ion by a simple dispersion formula (1), then the constant C would have the same value in this set, namely its value for neon. It may be recalled that on the usual theory, C measures the equivalent dispersion charge of the resonator. The diminution in the values of p_0 in each set is in accordance with the decreasing charge on the nucleus compared with the inert gas ; the ionic radius increases, the outer shell of electrons may be regarded as more loosely bound, and hence the increased refractivity.

General Dispersion Formula for a Gas.

3. Consider a gas composed of N similar molecules per unit volume; take O(x, y, z) as axes fixed in space, and let $(E_x, E_y, E_z)e^{ipt}$ be the electric force in the incident light wave. For any particular molecule take axes O′(ξ, η, ζ) fixed in the molecule. Let there be an isotropic resonator at the point (ξ_r, η_r, ζ_r), and let its electric moment be $(u_r, v_r, w_r)e^{ipt}$, referred to these axes; then, if there were no other resonators, we should have three equations of the form

$$a_r(p_r^2 - p^2)u_r = E_\xi, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the right-hand side being the components of force along the ξ, η, ζ axes. We have, however, to add the force at this point due to the moments of all the other resonators in the molecule; the ξ-component is

$$\Sigma_s \left[-\left\{ \frac{1}{d_{rs}^3} - \frac{3(\xi_r-\xi_s)^2}{d_{rs}^5} \right\} u_s + 3\frac{(\xi_r-\xi_s)(\eta_r-\eta_s)}{d_{rs}^5} v_s \right.$$
$$\left. + 3\frac{(\xi_r-\xi_s)(\zeta_r-\zeta_s)}{d_{rs}^5} w_s \right], \quad (3)$$

where the summation extends over the remaining resonators, and

$$d_{rs}^2 = (\xi_r-\xi_s)^2 + (\eta_r-\eta_s)^2 + (\zeta_r-\zeta_s)^2.$$

There are similar expressions for the η- and ζ-components; thus, if there are n resonators, we obtain, from (2) and (3), $3n$ equations, and the next step is to solve these for Σu, Σv and Σw in terms of E_ξ, E_η, and E_ζ. From these we then, in general, write down the components of molecular polarization U, V, W for the fixed axes O(x, y, z) in terms of E_x, E_y, E_z and the relative direction cosines of the two sets of axes; and finally we obtain the mean values of the U, V, and W for all possible orientations of the molecules, and so can specify the optical properties of the medium.

The immediate applications are simplified by the fact that we can choose molecular axes which are principal axes so that the solution of equations (2) and (3) is of the form

$$\Sigma u = \alpha E_\xi, \quad \Sigma v = \beta \Sigma_\eta, \quad \Sigma w = \gamma E_\zeta. \quad . \quad . \quad (4)$$

The medium as a whole is isotropic, and the averaging process gives for the refractive index

$$n^2 - 1 = \tfrac{1}{3}(A + B + C), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $$(A, B, C) = (4\pi N/3) \,.\, (\alpha, \beta, \gamma).$$

Further, in this simple case the scattering ratio, which is the ratio of the weak component to the strong in transversely scattered light, is given by

$$\rho = \frac{2(A^2+B^2+C^2-BC-CA-AB)}{4(A^2+B^2+C^2)+BC+CA+AB}. \quad . \quad . \quad (6)$$

For a symmetrical molecule with C = B, this reduces to

$$\rho = 2(A-B)^2/(4A^2+2AB+9B^2). \quad . \quad . \quad . \quad (7)$$

It should be noted that we are dealing only with a gas, and we have ignored the effect at any resonator in a molecule due to the remaining molecules; for a liquid we could add on the right of equations (2) and (3) the usual Lorentz term equal to one-third of the mean polarization, and so obtain a dispersion formula with $(n^2-1)/(n^2+2)$ taking the place of n^2-1.

4. For a diatomic molecule the separate equations need not be written down here; they lead at once to the result

$$R = n^2-1 = \tfrac{1}{3}(A+2B),$$

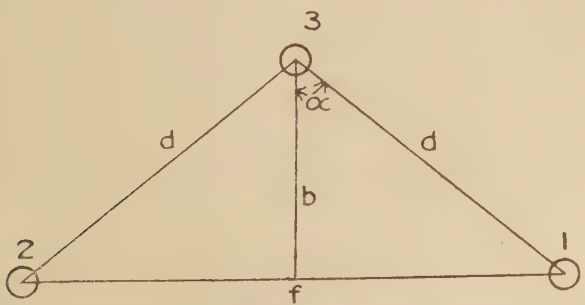
with

$$A = \frac{R_1+R_2+2kR_1R_2}{1-k^2R_1R_2},$$

$$B = \frac{R_1+R_2-kR_1R_2}{1-\frac{1}{4}k^2R_1R_2}. \quad . \quad . \quad . \quad . \quad (8)$$

In this we have put

$R_1 = 4\pi N a_1/(p_1^2-p^2)$; $R_2 = 4\pi N a_2/(p_2^2-p^2)$; $k = 1/2\pi N d^3$, where d is the distance between the two centres. We may note that if we interpret the resonator as an equivalent vibrating charge e of mass m, we should have $a = e^2/m$. R_1 and R_2 would be the refractivity of the gas if it were composed of monatomic molecules of the corresponding type separately.



5. For a triatomic molecule we shall need the symmetrical structure shown in the diagram, the atoms, or ions, at the

points 1 and 2 being alike. Taking the ξ-axis parallel to the line 12, the η-axis in the plane of the triangle, and the ζ-axis at right angles to the plane, the equations derived from (2) and (3) are

$$\mathrm{P}_1 u_1 = \mathrm{E}_\xi + \frac{2}{f^3} u_2 - \left(\frac{1}{d^3} - \frac{3}{4}\frac{f^2}{d^5}\right) u_3 - \frac{3bf}{2d^5} v_3,$$

$$\mathrm{P}_1 v_1 = \mathrm{E}_\eta - \frac{1}{f^3} v_2 - \frac{3bf}{2d^5} u_3 - \left(\frac{1}{d^3} - \frac{3b^2}{d^5}\right) v_3,$$

$$\mathrm{P}_1 w_1 = \mathrm{E}_\zeta - \frac{1}{f^3} w_2 - \frac{1}{d^3} w_3,$$

$$\mathrm{P}_1 u_2 = \mathrm{E}_\xi + \frac{2}{f^3} u_1 - \left(\frac{1}{d^3} - \frac{3}{4}\frac{f^2}{d^5}\right) u_3 + \frac{3bf}{2d^5} v_3,$$

$$\mathrm{P}_1 v_2 = \mathrm{E}_\eta - \frac{1}{f^3} v_1 + \frac{3bf}{2d^5} u_3 - \left(\frac{1}{d^3} - \frac{3b^2}{d^5}\right) v_3,$$

$$\mathrm{P}_1 w_2 = \mathrm{E}_\zeta - \frac{1}{f^3} w_1 - \frac{1}{d^3} w^3,$$

$$\mathrm{P}_2 u_3 = \mathrm{E}_\xi - \left(\frac{1}{d^3} - \frac{3f^2}{4d^5}\right) u_1 - \frac{3bf}{2d^5} v_1 - \left(\frac{1}{d^3} - \frac{3f^2}{4d^5}\right) u_2 + \frac{3bf}{2d^5} v_2,$$

$$\mathrm{P}_2 v_3 = \mathrm{E}_\eta - \frac{3bf}{2d^5} u_1 - \left(\frac{1}{d^3} - \frac{3b^2}{d^5}\right) v_1 + \frac{3bf}{2d^5} u_2 - \left(\frac{1}{d^3} - \frac{3b^2}{d^5}\right) v_2,$$

$$\mathrm{P}_2 w_3 = \mathrm{E}_\zeta - \frac{1}{d^3} w_1 - \frac{1}{d^3} w_2, \quad \ldots\ldots\ldots\ldots \quad (9)$$

where $\mathrm{P}_1 = a_1(p_1^2 - p^2)$ for the two like atoms,

and $\mathrm{P}_2 = a_3(p_2^2 - p^2)$.

Here we find that these equations give the molecular polarization in the form (4). Carrying out the solution as indicated in § 3, we obtain eventually

$$n^2 - 1 = \tfrac{1}{3}(\mathrm{A} + \mathrm{B} + \mathrm{C}),$$

$$\left(1-\frac{k\mathrm{R}_1}{16\sin^3\alpha}\right)$$

$$\times\left\{2\mathrm{R}_1+\mathrm{R}_2-\tfrac{1}{2}k\mathrm{R}_1\mathrm{R}_2\left(\frac{1}{4\sin^3\alpha}+4-12\sin^2\alpha\right)\right\}$$

$$\mathrm{A}=\frac{-9k^2\mathrm{R}_1{}^2\mathrm{R}_2\sin^2\alpha\cos^2\alpha}{\left(1-\frac{k\mathrm{R}_1}{16\sin^3\alpha}\right)\left\{1-\frac{k\mathrm{R}_1}{8\sin^3\alpha}-\tfrac{1}{2}k^2\mathrm{R}_1\mathrm{R}_2(1-3\sin^2\alpha)^2\right\}}$$

$$-\tfrac{9}{2}k^2\mathrm{R}_1\mathrm{R}_2\left(1-\frac{k\mathrm{R}_1}{8\sin^3\alpha}\right)\sin^2\alpha\cos^2\alpha$$

$$\left(1+\frac{k\mathrm{R}_1}{8\sin^3\alpha}\right)$$

$$\times\left\{2\mathrm{R}_1+\mathrm{R}_2+\tfrac{1}{2}k\mathrm{R}_1\mathrm{R}_2\left(\frac{1}{8\sin^3\alpha}-4+12\cos^2\alpha\right)\right\}$$

$$\mathrm{B}=\frac{-9k^2\mathrm{R}_1{}^2\mathrm{R}_2\sin^2\alpha\cos^2\alpha}{\left(1+\frac{k\mathrm{R}_1}{8\sin^3\alpha}\right)\left\{1+\frac{k\mathrm{R}_1}{16\sin^3\alpha}-\tfrac{1}{2}k^2\mathrm{R}_1\mathrm{R}_2(1-3\cos^2\alpha)^2\right\}}$$

$$-\tfrac{9}{2}k^2\mathrm{R}_1\mathrm{R}_2\left(1+\frac{k\mathrm{R}_1}{16\sin^3\alpha}\right)\sin^2\alpha\cos^2\alpha,$$

$$\mathrm{C}=\frac{2\mathrm{R}_1+\mathrm{R}_2+\frac{1}{2}k\mathrm{R}_1\mathrm{R}_2\left(\frac{1}{8\sin^3\alpha}-4\right)}{1+\frac{k\mathrm{R}_1}{16\sin^3\alpha}-\frac{1}{2}k^2\mathrm{R}_1\mathrm{R}_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Here α is the semi-angle between the radii from the central atom to the two like atoms, and the notation for R_1, R_2, and k is the same as in (8).

The particular case of the straight-line structure is deduced by putting $\alpha=\pi/2$, and we then obtain

$$n^2-1=\tfrac{1}{3}(\mathrm{A}+2\mathrm{B}),$$

$$\mathrm{A}=\frac{2\mathrm{R}_1+\mathrm{R}_2+\frac{3}{8}\frac{1}{k}\mathrm{R}_1\mathrm{R}_2}{1-\frac{1}{8}k\mathrm{R}_1-2k^2\mathrm{R}_1\mathrm{R}_2},$$

$$\mathrm{B}=\frac{2\mathrm{R}_1+\mathrm{R}_2-\frac{3}{16}\frac{1}{k}\mathrm{R}_1\mathrm{R}_2}{1+\frac{1}{16}k\mathrm{R}_1-\frac{1}{2}k^2\mathrm{R}_1\mathrm{R}_2}. \quad . \quad . \quad . \quad . \quad (11)$$

The Halogen Hydrides.

6. *HCl.*—As we shall use Cuthbertson's values of the refraction throughout, we shall adopt 5461 Å. as a convenient

standard wave-length which occurs in all his measurements. The value for HCl, under standard conditions, is

$$R = n^2 - 1 = 8{\cdot}96201 \times 10^{-4}. \quad . \quad . \quad . \quad (12)$$

For the scattering ratio ρ we use some recent observations by Ramanathan and Srinivasan *, who have measured the imperfection of polarization of scattered light for the three gases, HCl, H_2S, and NH_3; for all these they found that ρ has the same value 0·008. It should be noted that these writers point out that the gases CH_4, NH_3, H_2O may be expected to approach neon, while SiH_4, PH_3, H_2S, and HCl would approach argon. With this value of ρ we find from (7) that

$$A/B = 1{\cdot}27. \quad , \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The value of ρ is small, and we are not in a position to take any account of its variation with wave-length, so we shall simply use this value for our standard wave-length 5461.

From (8) and (13) we obtain

$$R_1 + R_2 = \frac{26{\cdot}886 + 64{\cdot}4\,k}{3 + 8{\cdot}891\,k},$$

$$R_1 R_2 = \frac{2{\cdot}226}{k(3 + 8{\cdot}391\,k)}, \quad . \quad . \quad . \quad . \quad (14)$$

where we have written R for $10^4 R$ and k for $10^{-4}k$. We might consider the distance d as one of the unknowns, but we have some guide to its value. It is generally assumed, from the theory of band spectra and other calculations, that the distance of the hydrogen nucleus from the centre of the chlorine ion is given by

$$d = 1{\cdot}17 \times 10^{-8}\ \text{cm}. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Using this value for d, and the standard value for N, we have

$$10^{-4}k = 0{\cdot}2865, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and, from (14), we find

$$R_1 = 0{\cdot}175 \times 10^{-4}; \quad R_2 = 8{\cdot}2145 \times 10^{-4}. \quad . \quad (17)$$

It is of interest to see how the values alter if we vary the value of d, and the following table shows the result :—

* K. R. Ramanathan and N. C. Srinivasan, Phil. Mag. i. p. 491 (1926).

$10^8 d$	1·433	1·33	1·27	1·252
$10^{-4} k$	0·2	0·25	0·2865	0·3
$10^4 R_1$	0·29	0·213	0·175	0·164
$10^4 R_2$	8·211	8·22	8·215	8·211

It seems that there is little variation in R_2, as it has a maximum in this range, but the relative change in R_1 is considerable; for this, and other reasons, it is not possible to calculate the dispersion of the ions, and we shall only deduce the refractivities at the chosen wave-length.

Assuming, then, the value of d in (15), we have the refractivities given in (17); it should be noted that these rest upon the experimental value 0·008 for ρ. Obviously the smaller value in (17) belongs to the hydrogen part of the molecule and the larger to the chlorine part. On the present view these would be best expressed simply by the the notation H^{Cl} and Cl^{H}, rather than the usual H^+ and Cl^-. Although the electron of the hydrogen atom must be regarded as completing effectively the outer shell of the chlorine ion, yet we assume the hydrogen part of the molecule to retain some small degree of polarisability; from (17) the molecular refractivity of H as it occurs in HCl is 0·13, while from the calculations mentioned in § 1 we find that the molecular refractivity of H in the homo-polar condition of H_2 is 1·0 at the same wave-length. For comparison we turn the values in (17) into molecular refractivities; in the usual notation,

$$R(\text{mol.}) = \frac{n^2-1}{n^2+2}\frac{M}{d} = 7470(n^2-1), \quad \text{approx. for gases.}$$

This gives for R(mol), reverting to the usual ionic notation for convenience,

$$H^+ = 0{\cdot}131\,; \quad Cl^- = 6{\cdot}136. \quad . \quad . \quad . \quad (18)$$

The value of HCl is 6·695, and the difference between this and the sum of the numbers in (18) is a measure of the interaction of the two units.

The value in (18) is much less than those previously assigned to Cl^-, which have been estimated from salts such as NaCl, KCl. A value usually given is 9·00, for the wave-length 5890. In discussing this value in relation to HCl and the assumption that the refractivity of H^+ is zero, Fajans and Joos* remark that the latter assumption is

* K. Fajans and G. Joos, *Zeit. für Phys.* xxiii. p. 15 (1924).

doubtful, as the hydrogen nucleus appears to have in the halogen hydrides a variable negative refractivity.

An average value for Cl^- given by Born and Heisenberg* is 7·74 (for $\lambda=\infty$), but they express their results in terms of deformability α, defined by

$$\alpha = \frac{3}{4\pi N_L}\frac{n^2-1}{n^2+2},$$

which gives $\alpha = 2{\cdot}94\times10^{-24}(n^2-1)$ approximately for gases. Their values for Cl^-, derived from the Li, Na, and K salts, are, respectively,

$$10^{24}.\alpha = 2{\cdot}84,\ 3{\cdot}05,\ 3{\cdot}25. \quad . \qquad (19)$$

The value in (17) for Cl^-, derived from HCl, gives

$$10^{24}.\alpha = 2{\cdot}42, \quad . \quad . \qquad (20)$$

a value which takes its place at the head of the series in (19).

The systematic variation in refractivity of the same ion, shown for example in the series of values in (19), has been remarked by various writers; it follows that the ion is not exactly the same in different crystal structures, but undergoes an isotropic compression or dilatation, even although the effect of the polarity of neighbouring ions should sum to zero. Born and Heisenberg, and other writers, consider a molecule such as HCl to be in a different category in that the hydrogen nucleus is within the electron shell of the chlorine ion, and its effect must therefore be extremely complicated. This may well be the case, though it may be pointed out that there is considerable variation in the estimates of the so-called ionic radius, according to the source of the data and the particular property which is being expressed by an equivalent radius of the ion; however this may be, it seems, on comparing the series of values in (20) and (19), that the difference is one of degree rather than of essential character. As a rough approximation we may divide the effect of neighbouring ions into two parts. One effect is isotropic and may be pictured as a uniform compression or dilatation, or, if we prefer, as an alteration in the effective charge on the nucleus; of this no theoretical explanation has been given, and we are not considering it specially here. The other part is anisotropic in its effect, in general, and we are treating it as due to the interaction of polarized elements; this is naturally only an approximate representation, but it enables us to bring into consideration the phenomena of scattered light.

* M. Born and W. Heisenberg, *Zeit. für Phys.* xxiii. p. 388 (1924).

7. It has been remarked that, assuming the refractivities R_1 and R_2 to be expressible by simple dispersion formulæ such as (1), the data do not warrant any direct evaluation of constants involved. It has been suggested in § 2 that the constant C may have the same values for the series Ar, Cl^-, S^{--}, and so on; if that is the case, then from the value in (17) we obtain a dispersion formula for Cl^- as deduced from HCl, namely

$$R_2 = 9{\cdot}4326 \times 10^{27} / (11784{\cdot}7 \times 10^{27} - p^2). \quad . \quad (21)$$

8. *HBr.*—The experimental value for the refractivity R at 5461 is $12{\cdot}3018 \times 10^{-4}$; also the distance of the hydrogen nucleus from the centre of the bromine ion is 1·41 Å., which gives

$$10^{-4} . k = 0{\cdot}21. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

For HCl we had also an experimental value for the ratio ρ for the polarization of scattered light; and, on the assumptions of the theory, these data sufficed to give definite values for R_1 and R_2.

For HBr there is no experimental value of ρ, and hence some additional assumption is necessary. The simplest plan seems to be to take the refractivity of the hydrogen part to be the same in this series of compounds.

Assuming $R_1 = 0{\cdot}175 \times 10^{-4}$, we obtain from (8) for Br^- the value

$$R_2 = 11{\cdot}5454 \times 10^{-4}. \quad . \quad . \quad . \quad . \quad (23)$$

With these values the ratio ρ works out as 0·005. The smaller value might be expected from the larger refractivity of Br^- and from the greater distance between the centres; if the experimental value proves to be different, either the refractivity of the hydrogen or the distance apart might be modified.

The same comparisons may be made as in the previous section. From (23) the molecular refractivity is 8·624; the values usually given range from 12·67 to 9·9. The values of the deformability α given by Born and Heisenberg for Br^-, derived from the Li, Na, and K salts respectively, are

$$10^{24} . \alpha = 3{\cdot}90,\ 4{\cdot}16,\ 4{\cdot}45. \quad . \quad . \quad . \quad (24)$$

From (23) we find for Br^-, derived from HBr,

$$10^{24} . \alpha = 3{\cdot}40. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

We are unable to complete the series of halogen hydrides

for lack of data. We do not know the refractivity of HF, and there is no estimate of the distance d for HI; further, we have no observations of the polarization of scattered light in either case.

Triatomic Molecules.

9. We shall consider now some triatomic molecules in which two of the atoms are similar. One of the questions of molecular structure which has been under discussion recently is whether the three units lie in a straight line or at the corners of a triangle. One method of attack is the examination of mutual potential energy and the stability of equilibrium; other relevant considerations are the permanent electric moment of the molecule, and its moments of inertia as deduced from infra-red band spectra. Here we are considering only the optical anisotropy of isotropic units arranged in a certain configuration, and the dispersion formulæ we need have been given in equations (10) and (11).

10. CO_2—We shall consider this gas first because more information is available. For the refractivity at the wave-length 5461 we have

$$R = n^2 - 1 = 9{\cdot}01203 \times 10^{-4}, \quad . \quad . \quad . \quad (26)$$

and for the scattering ratio we take

$$\rho = 0{\cdot}11, \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

being a mean of the values 0·108 and 0·117 given by Rayleigh and Raman & Rao respectively. Various estimates of the structure of the molecule have been put forward. A recent one by Dennison * is based on an analysis of the infra-red band spectrum; the computed structure is an isosceles triangle with each oxygen nucleus at a distance 0·96 A. from the carbon nucleus, and the latter at a distance of 0·3 A. from the centre of gravity of the oxygen nuclei. Thus the angle α of the figure in § 5 is about 72°. For arguments in favour of a straight-line model, reference may be made to a subsequent paper by Eucken †.

Here we shall assume for simplicity a straight-line, symmetrical, model; in any case a semi-angle of 72°, instead of 90°, would make little difference to the optical effects which we are considering here.

* D. M. Dennison, Phil. Mag. i. p. 195 (1926).
† A. Eucken, *Zeit. für Phys.* xxxvii. p. 714 (1926).

The dispersion equations are given in (11) and we have, from (26) and (27),

$$A = 2{\cdot}44\ B. \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

We have two equations for the three quantities R_1, R_2, and k : the first two are the refractivities of the oxygen and carbon respectively, and k gives the distance d of each oxygen nucleus from the carbon nucleus. By choosing values of d we can solve the equations for corresponding pairs of values of R_1 and R_2. The following table shows sets of solutions obtained in this way :—

$10^8 d$.	$10^{-4} k$.	$10^4 R_1$.	$10^4 R_2$.
0·83	1·024	3·8	0
0·9	0·807	3·553	0·03
0·95	0·6861	3·454	0·061
1·0	0·588	3·388	0·101
1·1	0·442	3·313	0·149
1·5	0·1743	2·945	1·42
1·6	0·1436	2·658	2·15

Before deciding which set of values to adopt, two previous calculations may be mentioned. W. L. Bragg * assumes the distance d to be 1·3 Å., and further supposes the refractivity of the carbon to be zero ; he then deduces for the oxygen a refractivity $4{\cdot}42 \times 10^{-4}$ (in the notation used here). But he takes no account of the scattering ratio, and, in fact, if we work out ρ from his values, we get about 0·008 instead of the experimental value 0·11.

From the first line of the table just given we see that, assuming the carbon refractivity to be zero, we can only satisfy the refraction and scattering of the molecule with $d = 0{\cdot}83$ Å. and the oxygen refractivity $3{\cdot}8 \times 10^{-4}$.

Another calculation is that of Ramanathan †, who used the refractivity and scattering ratio of the gas and deduced the distance d. For that purpose he assumed the carbon refractivity to be the same as in diamond, namely $2{\cdot}841 \times 10^{-4}$, and the oxygen refractivity to be the same as

* W. L. Bragg, Proc. Roy. Soc. A, cvi. p. 366 (1924).
† K. R. Ramanathan, *loc. cit. ante.*

in the molecule O_2, namely $2{\cdot}384 \times 10^{-4}$; the values of d is then 1·66 Å. But this does not seem a reasonable assumption for the refractivities.

It may be taken that the carbon is in the state C^{4+} and the oxygen as O^{--}. The carbon, having the helium structure with additional nuclear charge, will certainly have a very small refractivity. The molecular refractivity of helium at the D-line is 0·5; and Fajans and Joos, in the paper quoted in § 6, estimate the values for the series Li^{+}, Be^{++}, B^{3+}, C^{4+} as 0·2, 0·1, 0·05, and 0·03 respectively. Turning to the table given above, for the present calculations we shall select for C^{4+} the value $R_2 = 0{\cdot}061 \times 10^{-4}$, or a molecular refractivity of 0·045. The corresponding value for O^{--} is $3{\cdot}454 \times 10^{-4}$, and the molecular refractivity and deformability are

$$R\,(\text{mol.}) = 2{\cdot}58\,; \quad 10^{24}\alpha = 1{\cdot}016. \quad . \quad . \quad (29)$$

These values are again considerably lower than those previously assigned to O^{--}, which have usually been calculated on the assumption that refractivity is additive.

From the table we have the distance $d = 0{\cdot}95$ Å., and this may be compared with Dennison's estimate of 0·96 A., although the latter refers to an obtuse-angled form.

11. CS_2.—This molecule may be supposed similar to that of CO_2, and it has also a large scattering ratio: we shall take as a mean of experimental values

$$\rho = 0{\cdot}145. \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

The refractivity, at the D-line, is given as

$$R = n^2 - 1 = 29{\cdot}542 \times 10^{-4}. \quad . \quad . \quad . \quad (31)$$

For a straight-line model we have equations (10); and, as in the previous section, we calculate sets of corresponding values of d, R_1, and R_2. They are shown in the following table:—

$10^8 d$.	$10^{-4} k$.	$10^4 R_1$.	$10^4 R_2$.
1·2	0·34	11·21	0·032
1·23	0·3143	10·96	0·061
1·3	0·2677	10·57	0·1
1·5	0·1743	10·01	0·56

Taking the carbon to have the same refractivity as in CO_2, we get $d = 1{\cdot}23$ Å. for the distance between the carbon nucleus and either sulphur nucleus: further, the refractivity of S^{--} is $10{\cdot}96 \times 10^{-4}$, or

$$R\,(\text{mol.}) = 8{\cdot}19. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

12. *H_2S.*—Returning now to the series of hydrides, we have for H_2S at 5461,

$$R = n^2 - 1 = 12{\cdot}8842 \times 10^{-4}, \quad . \quad . \quad . \quad (33)$$

and the value given by Ramanathan and Srinivasan,

$$\rho = 0{\cdot}008. \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Assume, in the first place, a symmetrical straight-line model, and we use equations (11) again. Further, we shall suppose the hydrogen to have the same refractivity as we deduced from HCl, namely

$$10^4 R_1 = 0{\cdot}175. \quad . \quad . \quad . \quad . \quad . \quad (35)$$

The solution of the equations is

$$10^{-4} k = 0{\cdot}1553\,; \quad 10^4 R_2 = 10{\cdot}979 \quad . \quad . \quad (36)$$

We note that this value of k gives

$$d = 1{\cdot}56\,\text{Å}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

for the distance of either hydrogen nucleus from the sulphur nucleus. Further, the refractivity of S^{--} in (28) is practically the same as we obtained in the previous section from CS_2.

This straight-line model gives no permanent electric moment for the molecule. A triangular form has been suggested recently by Hund* derived from certain considerations of stability; in it the distance between either hydrogen nucleus and the sulphur nucleus is 1·5 Å., and the distance between the two hydrogen nuclei 1·6 Å.

It will be sufficient for our purpose to examine an equilateral form of side 1·55 Å. and to take $\alpha = 30°$ in the general dispersion equations (10). We shall state the solutions briefly, without repeating all the numerical work here. With the given value of d we have $10^{-4} k = 0{\cdot}158$. Putting the values of k and α in (10), we obtain the quantities A, B,

* F. Hund, *Zeits. für Phys.* xxxi. p. 81 (1925); also xxxii. p. 1 (1925).

C expressed in terms of R_1 and R_2, which are now the two unknown quantities; and the equations to be solved are

$$A+B+C = 38{\cdot}6526,$$

$$\frac{2(A^2+B^2+C^2-BC-CA-AB)}{4(A^2+B^2+C^2)+BC+CA+AB} = 0{\cdot}008, \quad . \quad (38)$$

omitting some obvious powers of 10.

These can only be solved by trial and approximation. Suppose we try first the hydrogen refractivity the same as in HCl, namely $R_1 = 0{\cdot}175$. Then we find we can satisfy the first equation in (38), that is, we can make the molecule have the proper refractivity, with

$$R_2 = 11{\cdot}86, \quad A = 12{\cdot}614, \quad B = 14{\cdot}179, \quad C = 11{\cdot}858.$$

But with these values of A, B, and C the second equation of (38) is not satisfied; for we obtain $\rho = 0{\cdot}0034$ instead of $0{\cdot}008$. We find by trial that in order to satisfy both equations in (38) it is necessary to take $R_1 = 0{\cdot}5$ approximately. But this seems too great a divergence from the value we found from HCl. We may consider the hydrogen to be similar in the two molecules; and although some difference may be expected, it seems reasonable to assume that the refractivity is approximately the same. If this is the case, we may conclude that Hund's model does not agree with the observed state of polarization of scattered light; without going into the details of Hund's calculation, it may be remarked that it involves the deformability of S^{--}, for the systems he considers are a strongly polarizable negative ion together with one or more unpolarizable positive ions. Here we are attempting to deduce the refractivity of both ions from optical considerations. No doubt it would be possible to adjust the distances between the ions so as to give a triangular form satisfying the optical conditions, with reasonable values of the refractivities; but these conditions are not in themselves sufficient to determine the form, therefore it is not worth while pursuing the matter further without bringing in other considerations, such as stability, electric moment, and so forth. We leave it for the present with the remark that the simple straight-line model fits these optical considerations with reasonable distances between the ions and with refractivities agreeing with those found from similar structures.

13. H_2O.—In this case we have still less information available, for we have no experimental value for the polarization of scattered light. The refractivity, at 5461, reduced to standard conditions is

$$R = n^2 - 1 = 5{\cdot}05463 \times 10^{-4}. \quad . \quad . \quad . \quad (39)$$

The agreement found in the previous sections for S^{--}, derived from a study of CS_2 and H_2S, suggests that we should now assume for the oxygen in H_2O the refractivity for O^{--} derived from CO_2. Taking also, as before, the same refractivity for the hydrogen, we have equations (11) with

$$10^4 R_1 = {\cdot}175\,; \quad 10^4 K_2 = 3{\cdot}454. \quad . \quad . \quad (40)$$

With the value (39) we can solve for k, and we find the value $0{\cdot}5533 \times 10^4$, which gives

$$d = 1{\cdot}02\,\text{A}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

for the distance of either hydrogen nucleus from the oxygen nucleus.

We can at the same time work out the polarization ratio for scattered light from these values, and we find

$$\rho = 0{\cdot}107. \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

Hund, in the paper already quoted, has put forward two possible triangular structures for the H_2O molecule.

In one model the distance from either hydrogen nucleus to the oxygen nucleus is 1·03 A., and the distance between the hydrogen nuclei 1·09 A. Let us assume the same value 0·175 for the hydrogen refractivity, then from equations (10) we can find the oxygen refractivity, and can also calculate the corresponding scattering ratio. We have in this case, omitting powers of 10 in certain cases,

$$k = 0{\cdot}5383\,; \quad \alpha = 32^\circ. \quad . \quad . \quad . \quad . \quad (43)$$

We obtain, with sufficient approximation, the solution

$$R_2 = 3{\cdot}72, \quad A = 4{\cdot}777, \quad B = 6{\cdot}649, \quad C = 3{\cdot}719. \quad (44)$$

These values of A, B, and C give a scattering ratio

$$\rho = 0{\cdot}033. \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

The other model is rather more open. The distance of either hydrogen nucleus from the oxygen nucleus is 1·01 A.,

and the angle $\alpha = 55°$. In the same way as before, we obtain the solution

$$R_2 = 3{\cdot}6, \quad A = 6{\cdot}728, \quad B = 4{\cdot}871, \quad C = 3{\cdot}556, \quad (46)$$

and these lead to

$$\rho = 0{\cdot}038. \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

It is of interest to note that in both these models the distance of a hydrogen nucleus from the oxygen nucleus is practically the same as we obtained from the straight-line model with the assumptions mentioned. We note the slightly higher oxygen refractivity necessary in the triangular forms to give the correct refractivity for the molecule as a whole. There is a considerable difference in the optical anisotropy, as measured by the scattering ratio ρ, and it would be of great interest to have an experimental value of this quantity for H_2O reduced to standard gaseous conditions.

Summary.

14. The paper deals with the refractivity of gases when the constituents of the molecule are treated as isotropic resonators in fixed relative positions in the molecule; formulæ are given for straight-line and triangular configurations. The gases specially examined are HCl, HBr, H_2S, H_2O, and CO_2, CS_2. For the series of hydrides an examination of empirical dispersion formulæ shows the relation of these gases to the corresponding inert gases. In addition to the refractivity of the gas, use is made of experimental values of the ratio of the two components of light scattered at right angles to an incident beam. For HCl, with the help of the distance between the nuclei inferred from the infra-red band spectrum, these data are sufficient to give values for the refractivities of the hydrogen and chlorine constituents of the molecule. With this value for the hydrogen refractivity and other data where available, a fairly consistent set of values is obtained for the other gases of the series; the molecular refractivities of the ions obtained by this method are $H^+ = 0{\cdot}13$, $Cl^- = 6{\cdot}14$, $Br^- = 8{\cdot}62$, $O^{--} = 2{\cdot}58$, $S^{--} = 8{\cdot}19$, $C^{4+} = 0{\cdot}045$. These are discussed in relation to values which have been obtained from other sources. Certain triangular forms which have been suggested for some of the molecules are examined from the point of view of refractivity and optical anisotropy.

XV. *The Measurement of Transmission and Reflexion of Sound by Partitions of Various Materials.—I. Felt-like Materials.* *By* A. H. Davis, *D.Sc., and* T. S. Littler, *M.Sc., Physics Department, The National Physical Laboratory* *.

Abstract.

The present paper is part of a study of the transmission and reflexion of sound by various partitions, and relates mainly to partitions of a felt-like nature. The method used is on the general lines of that due to F. R. Watson. The partition is clamped over an aperture in the wall between two adjacent sound-proof rooms, in one of which a source of sound, in conjunction with a paraboloidal mirror, directs a fairly uniform beam of sound obliquely on to the partition. Measurements of intensity are made in the transmitted and reflected beams and at various other points within the rooms. A description is given of the electrical equipment used in the production and measurement of the sound-field. The actual arrangement has the advantage that under certain conditions the exploration of the sound-field is not affected by inconstancy of the current operating the loud-speaker source, nor by gradual drift in the efficiency of the amplifiers employed. Tests were carried out to determine if there was any reaction on the source when a test material was placed over the aperture, but no appreciable effect was observed. A detailed study of the field of sound in the two rooms was made both with and without a partition over the aperture. The results of this exploration showed that transmission and reflexion ratios were almost independent of the positions in the beam at which the measurements were made. A number of partitions were tested, and the consistency of the results is indicated in graphical form. The transmission of sound through felt was specially investigated. Four partitions of hair-felt, each of 0·58 in. thickness, were employed, and the transmission through one, two, three, and four layers was studied. A number of frequencies ranging from 250 to 1600 vibrations per second were used, and curves are given showing the results obtained. A comparison is made between these results and those obtained by P. E. Sabine who used a reverberation method.

Introduction.

THE transmission of sound through a partition may take place in a variety of ways. The sound may pass through cracks or pores in the material; or it may set up in the material of the partition condensations and rarefactions which, transmitted from particle to particle in the wall, are

* Communicated by the Authors.

ultimately communicated as sound to the air on the opposite side; or the incident sound may set the partition in vibration as a whole, like a diaphragm, and so create sound-waves on the opposite side.

The relative importance of these phenomena depends upon the nature of the partition. It may be shown from a formula given by Rayleigh * that non-absorbent partitions of mahogany, two inches thick, if flexurally rigid, would transmit only a few parts in one million of the incident sound. Consequently, we may infer that drum-like vibration is mainly responsible for transmission through ordinary solid partitions, true acoustical transference playing but a negligible part. The natural frequency for drum-like vibration of any partition depends, not only upon its size and shape, but also upon the nature of the clamping at the edges. For a 2-inch mahogany board, 5 ft. × 4 ft. in area, supported at its edges, the gravest mode of vibration would have a frequency of about 85 vibrations per second †. If, as thus appears probable, the natural frequencies of a partition fall in the audible range, it is desirable for practical purposes to conduct transmission tests upon samples having a size and method of fixing comparable with that normally employed in building.

Various methods of study have been employed. W. C. Sabine ‡ used the well-known method which he developed from his pioneer work upon reverberation. The partition was built into an aperture in the wall between two adjacent rooms; a sound was produced in the larger and more reverberant room and then, on stopping the source, observation was made of the duration of audibility in each of the two rooms. Unfortunately, the method requires very large rooms and would usually involve the erection of a special building. F. R. Watson § adopted a different method in which the sound is incident on the partition at a definite obliquity. He does not give very full details of the difficulties arising in the work, but the method has the advantage that it requires only rooms of moderate size such as may frequently be found in basements of existing buildings.

The present paper forms part of a study, on the general lines of the Watson method, of transmission and reflexion of

* Rayleigh, 'Theory of Sound,' vol. ii. Art. 271, Equation (10).

† Calculated from formulæ given by Rayleigh, 'Theory of Sound,' vol. i. Art. 195, Equation (2); and Art. 217, Equation (1).

‡ W. C. Sabine, 'Calculated Papers,' p. 237. Harvard University Press, 1922.

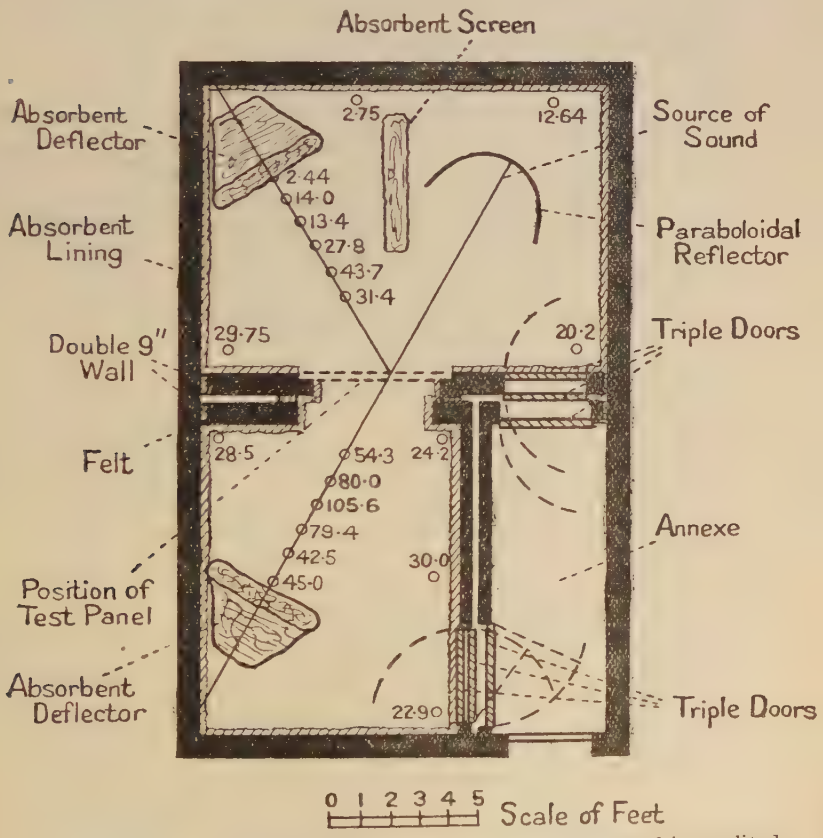
§ F. R. Watson, University of Illinois Engineering Experiment Station, Bulletin No. 127 (1922).

sound by partitions. The present results are limited mainly to felt-like materials. Consideration of solid partitions and of the complications which may arise from their drum-like vibration is reserved to a later paper.

General Description of Apparatus.

As already stated, the general method used for this work is based upon that described by Watson, and the disposition

Fig. 1.



Sound-proof rooms, and results of acoustic exploration, expressed in amplitudes.

of the apparatus used is shown in fig. 1. Partitions of the test material, 5 ft. × 4 ft. in size, are clamped over an aperture in the wall between two adjacent sound-proof rooms. In

one a source of sound, in conjunction with a paraboloidal mirror 5 ft. in diameter, directs a fairly uniform beam of sound towards the test partition. Measurements of intensity are made on the axes of the transmitted and reflected beams respectively.

The sound-proof rooms, which are in a particularly silent situation, have walls about 2 ft. thick, concrete floors, and masonry ceilings. The wall between the two rooms is composed of two 9-inch brick walls, separated from each other by a 6-inch air-cavity and from the ceiling by a layer of felt. Apart from the test aperture, there is no direct communication between the rooms, and each is entered through three sound-proof doors from the annexe shown.

To reduce the intensity of sound in the region outside the main beams, and to minimise the occurrence of stationary waves, the walls, ceilings, and floors of the rooms have been covered with absorbent materials. Special attention has been paid to the corners towards which the sound-beams are directed, and absorbent deflectors inclined to the vertical at 45 degrees have been placed in these situations to reduce direct return of the sound along the path of the beam. In order to prevent stray sound from the source from interfering with the reflected beam, an absorbent screen has been placed in the centre of the source-room.

Measurements of intensity are normally made at every foot distance along the beams. To ensure that the same positions should always be used, a series of light bobs were suspended from the roof by silk threads to indicate them.

The source of sound used is an electrical loud-speaker operated by means of alternating current of approximately pure sinusoidal wave-form as generated by a valve oscillator.

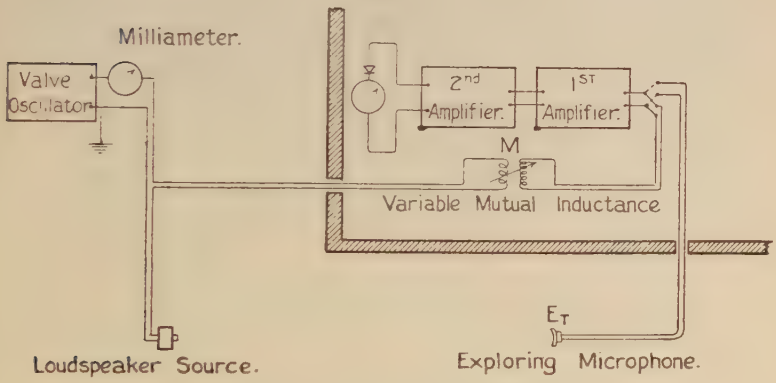
Telephonic apparatus is employed for measuring sound-intensity. In this use is made of the result that, for a constant frequency, the e.m.f. generated in the windings of a magnetophone placed in a sound-field is proportional to the pressure amplitude.

An electromagnetic microphone with an iron diaphragm was employed in the earlier work and was found to be very variable. Its performance was greatly improved when the diaphragm was clamped by means of a metal cap instead of the usual ebonite one. However, an electrodynamic loud-speaker of the moving-coil type proved so satisfactory as a microphone that it was adopted for the later work. Improvements in the source were found to be necessary later to ensure complete constancy. At present overall variations of 6 per cent. are met with from time to time.

Measurement of the e.m.f. generated by the Microphone.

The disposition of the complete electrical equipment for the production and measurement of the sound is shown diagrammatically in fig. 2. The loud-speaker is actuated by means of a thermionic valve oscillator giving a very good approximation to a sinusoidal wave-form. The microphone was connected through a two-way switch to the input of an amplifier system, which could be varied according to requirements, and consisted of from one to six valve stages. The output of the amplifier system was connected through a transformer to a crystal rectifier in series with a galvanometer. The rectifier, a zincite-bornite couple of fairly heavy

Fig. 2.



Disposition of electrical apparatus.

contact, was constant for very long periods. A galvanometer deflexion could thus be obtained, the magnitude of which was a measure of the small e.m.f. generated by the microphone.

To determine the actual value of this e.m.f. a substitution method was adopted *. By means of the two-way selector key mentioned, a variable e.m.f. from a mutual inductometer M could be substituted for that from the microphone, and its magnitude could be adjusted until an equal galvanometer deflexion was obtained. For a given frequency the actual value of this e.m.f. was calculable from the setting of the instrument and the magnitude of the current through its primary coil, as measured by the milliameter shown.

* *Cf.* Karcher, 'Bur. Stds. Sci. Papers,' No. 473, 1923.

By deriving the alternating current for the mutual inductometer direct from the loud-speaker circuit, it was automatically ensured that the known e.m.f. was of precisely the same frequency as the equal unknown e.m.f. from the microphone. With the two inputs to the amplifier system thus equal in magnitude and frequency, the characteristics of the amplifier system were not important. Nevertheless, the amplifier was carefully constructed, with resistance-capacity coupling designed to deal faithfully with the inputs obtained, and care was taken that none of the valves was overrun.

In operation, with the loud-speaker sounding, the microphone leads are switched into connexion with the input of the amplifier and the galvanometer deflexion noted. The switch is then changed over so that the secondary of the mutual inductometer is substituted for the microphone and the value (M) of the mutual inductance adjusted until, on switching quickly from one input to the other, the galvanometer deflexion remains unaltered. In this condition the e.m.f. (E_M) generated in the microphone and the standard e.m.f. (E_S) derived from the inductometer are equal.

If the alternating current, of frequency n, passing through the loud-speaker and through the inductometer be denoted by i, and if the sound-amplitude at the microphone be A, then we have

$$E_M = kA \text{ where } k \text{ is a constant for a given frequency,}$$

and $$E_S = 2\pi n M i.$$

Since we arrange these e.m.fs. to be equal, we have for a given frequency

$$A \propto Mi.$$

It is interesting that with this equipment it is not necessary to keep the electrical current i from the oscillator absolutely constant. This follows, since the mutual inductometer reading M is seen to be a measure of A/i. To the extent to which A/i is constant—and for good loud-speakers the amplitude A of the emitted sound may be proportional to the current i over a very wide range—the mutual inductometer reading M is thus a measure of the sound amplitude near the microphone arising from unit current through the loud-speaker. While it would then follow that the actual current i need not be measured, in practice it has been maintained at a constant measured value throughout each series of experiments.

Test for any Effect upon the Output from the Source, of the Sound reflected from the Test Partition.

As has been mentioned already, the loud-speaker itself was satisfactory in that it behaved in a constant manner under constant conditions. It is, however, well known that the energy emitted by a source of sound may depend upon the proximity of reflecting walls or upon its position in the room, since the output is affected by the acoustic condition of the air in its vicinity. In the present experiments it is regarded as essential that the acoustic output of the loud-speaker should remain the same whether the test partition were in position over the aperture or not. Owing to the general disposition of the apparatus, the obliquity of incidence of the beam of sound upon the partition, and the absorbent nature of the walls of the room, it was unlikely that sound reflected by a partition would greatly affect the acoustic condition of the air near the source. However, it was necessary to make tests on the matter.

In the first place a microphone was placed near the source, and measurements taken of the sound-intensity both before and after a standard partition of mahogany board was placed in position. Only a very slight difference was noticed, the amplitude being about 6 per cent. greater when the partition was in position.

This in itself does not necessarily mean that the output from the source has increased: it may merely mean that the intensity of sound generally diffused in the source-room has been increased somewhat by preventing the escape of sound to the second room. A further test was therefore carried out. If the acoustic impedance offered by the air to the motion of the loud-speaker diaphragm is altered, the changed load can be detected by change in the apparent electrical impedance of the instrument. An electrical bridge was therefore set up whereby change in the vector impedance of the loud-speaker could be measured. With the instrument emitting sound as in normal experiments, its vector impedance was measured with and without the test mahogany board in position. The instrument had an inductance of about 2·2 henries and a resistance of about 3300 ohms. No measurable change in reactance of the loud-speaker was experienced, any variation certainly being less than about 1/3 of 1 per cent. A small change in the resistance did not exceed one part in 3600.

It appears clear that no appreciable error arises in the experiments from changed output of the source.

Preliminary Exploration of the Rooms.

The field of sound in the two chambers was explored. Measurements were made at distances 1 ft., 2 ft., ... 8 ft. from the aperture in the reflected and transmitted beams respectively, and also, outside these beams, at various other points, for which results are shown as amplitudes on an arbitrary scale in fig. 1.

Expressing the results in terms of sound-energy by squaring the amplitude data, we find that in the reflexion room the general intensity in positions screened from direct radiation from the loud-speaker is only about 0·13 per cent. to 4 per cent. of the intensity in the transmitted beam. In the tests of partitions described later, results were utilized from the three farthest positions along the reflected beam, as these were most shielded.

In the transmission-room the intensity of stray sound outside the beam varies from 11 per cent. of the mean to 20 per cent. It will be noted that some positions of reduced intensity (nodes) still occur in the length of the beam, the energy varying about ± 50 per cent. from the mean : in spite of this, however, it will be seen later that transmission coefficients obtained for a given material were largely independent of the position in the beam at which the measurement was made. An exploration was made across the width of the beam at the 5-feet position, measurements being taken at 6-inch intervals. The results obtained are shown in fig. 3, where it will be seen that the main beam is moderately uniform over a width of about 2 feet.

Preliminary Tests with various Materials.

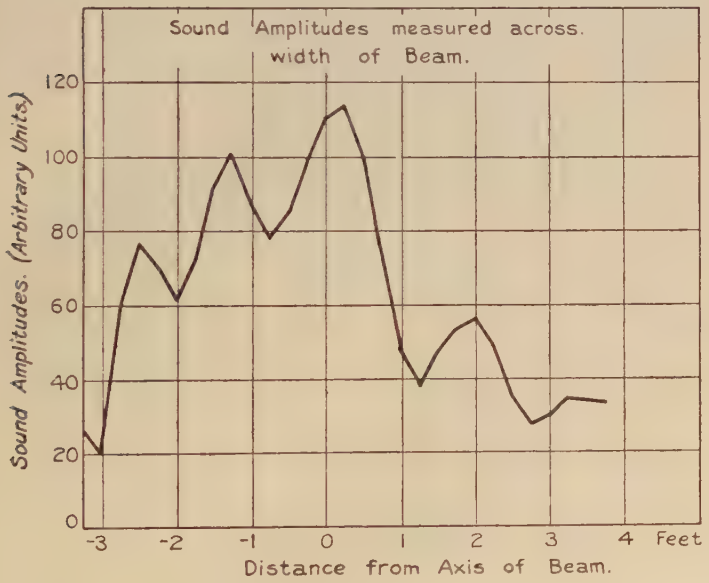
In the test of a partition clamped over the aperture, a series of readings was taken in the transmitted and reflected beams at positions which were exactly the same as those adopted with the uncovered aperture.

A series of partitions of different kinds was tested, the source having a frequency of 700 vibrations per second. Some preliminary work with a frequency of about 2000 showed that for sound of short wave-length it was important that the test material (felt, etc.) be stretched over the aperture to avoid convexities or concavities of its surface and the consequent focussing effects. Indeed, on pushing the felt somewhat out of its original shape, reflexion readings could be markedly affected ; the effect on the transmission, while perceptible, was naturally much less. However, it was found that for sounds of frequency 700 such differences were not

very appreciable, and no elaborate precautions were taken to maintain the surfaces accurately plane.

It has been mentioned above that in the earlier work the sensitivity of the loud-speaker and of the sonometer varied somewhat from day to day. To allow for any error due to such cause, a series of readings for a standard condition was taken both immediately before and immediately after the test of the partition. Naturally, the condition of uncovered aperture was adopted as a standard for this purpose ; but in some cases it was more convenient to utilize a good reflector as standard, and a 2-inch mahogany board was then used.

Fig. 3.

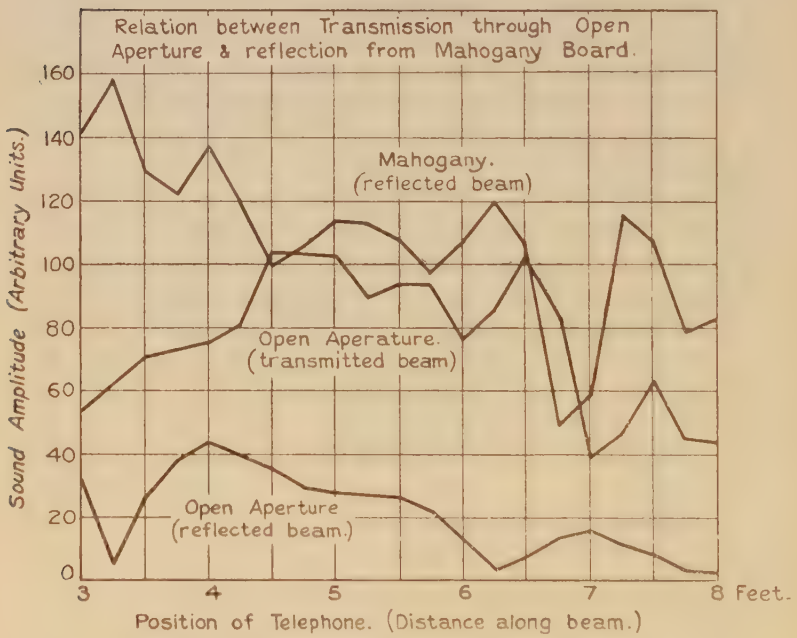


A special series of experiments was conducted to determine the relation between the sound reflected from the standard mahogany board and that transmitted through the open aperture. Readings were taken at especially frequent intervals (every 3 inches) along the respective beams, and the results are given in fig. 4. The abscissæ represent distances along the beam measured from the front surface of the test material.

In order to determine the extent to which transmission and reflexion ratios were dependent on the points at which measurements were taken, experiments were conducted as

follows. A series of readings was taken every 3 inches along the beam, transmitted through the open aperture. A quilt material was then placed over the aperture and the process repeated, readings of intensity being taken at the same series of positions as before. The results of such an experiment are given in fig. 5. The abscissæ represent distances along the beam, and the ordinates represent the amplitude in arbitrary units, plotted on a logarithmic scale. The two

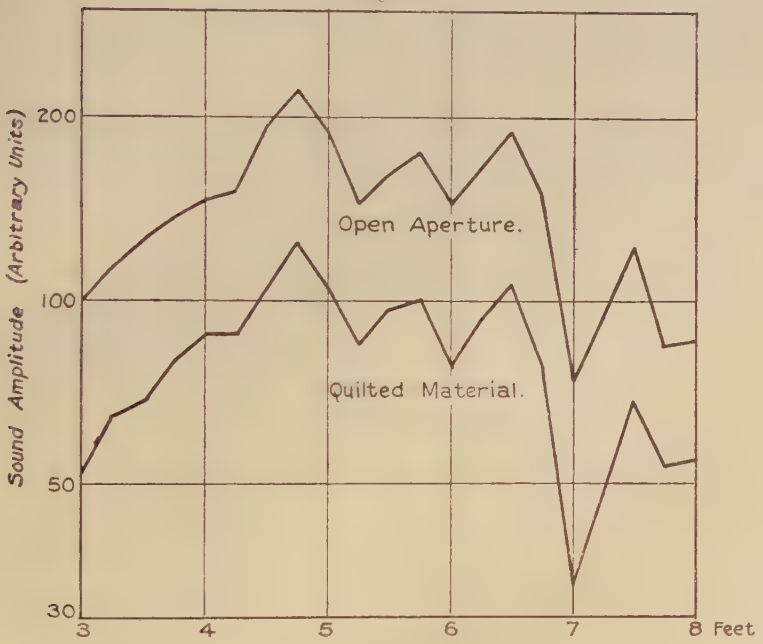
Fig. 4.



curves obtained are strikingly similar and are practically parallel. Since on a logarithmic scale equal distances between ordinates imply equal ratios, this parallelism of the two curves implies that the effect of covering the aperture with a layer of quilt material is to reduce the intensity of the transmitted sound everywhere in nearly the same ratio. In the case of the reflected beam, similar results were obtained Reflexion from a 2-inch mahogany board was taken as standard, and the effect of covering this with, say, a layer of felt was to reduce the intensity of the reflected beam in nearly the same ratio at all points of the beam.

The procedure referred to was carried out in a specially detailed manner for the two cases mentioned, measurements being taken every 3 inches along the beam. A whole series of partitions was then tested, the amplitude of the sound along the axis of the beam being measured for the normal series of positions 1 foot apart, the positions being defined by their distance from the front surface of the partition.

Fig. 5.



Exploration of transmitted beams.

In figs. 6 and 7 these results have been presented in the form of ratios to a standard condition. In fig. 6, for the usual series of positions, amplitudes of sound transmitted through various partitions are expressed as a fraction of the amplitude transmitted through the open aperture. Similarly, in fig. 7, amplitudes of reflected sound are expressed in terms of the reflexion from the standard mahogany board. Quite a high percentage of incident sound is reflected from such a board, and it is unlikely that the ratios obtained differ very appreciably from the values which would have resulted from the use of a perfect reflector.

Fig. 6.

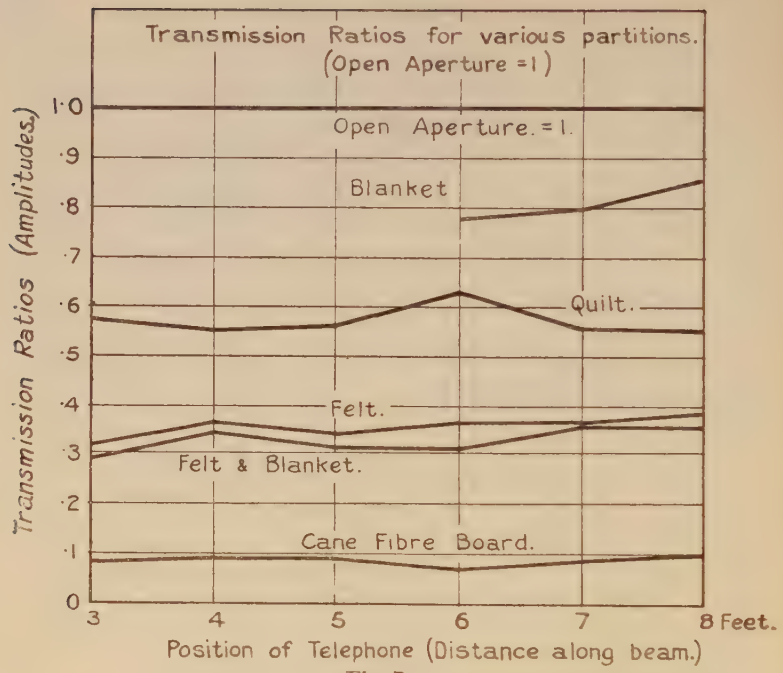

Transmission Ratios for various partitions.
(Open Aperture =1)
Transmission Ratios (Amplitudes)
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
0
Open Aperture. = 1.
Blanket
Quilt.
Felt.
Felt & Blanket.
Cane Fibre Board.
3
4
5
6
7
8 Feet.
Position of Telephone (Distance along beam.)

Fig. 7.

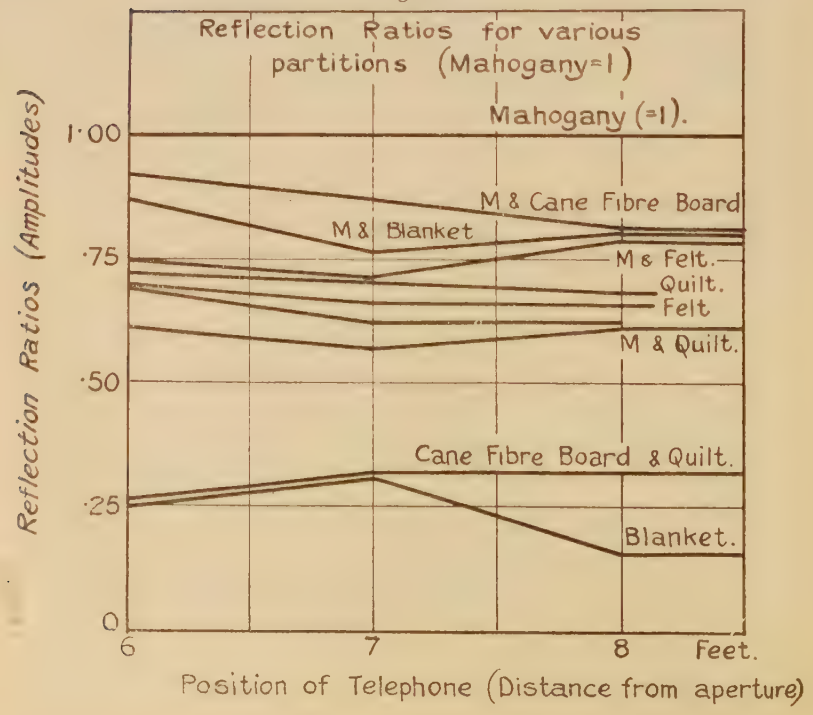

Reflection Ratios for various partitions (Mahogany=1)
Reflection Ratios (Amplitudes)
1·00
·75
·50
·25
0
Mahogany (=1).
M & Cane Fibre Board
M & Blanket
M & Felt.
Quilt.
Felt
M & Quilt.
Cane Fibre Board & Quilt.
Blanket.
6
7
8
Feet.
Position of Telephone (Distance from aperture)

TABLE I.

Acoustical Transmission and Reflexion Ratios for various Partitions.

(Frequency of source : 700 d.v.)

Partition.	Reflexion Ratio (Mahogany = 1). r.	Transmission Ratio (Open aperture = 1). t.
None	0·015	1·00
Mahogany 2 in.	1·00	0·00029
Eelgrass Quilt	0·50	0·32
Cane-fibre Board	.....	0·008
Felt	0·46	0·14
Felt + Blanket	0·42	0·12
Blanket	0·05	0·66
Composite partitions:—		
Mahogany 2 in. + Cane-fibre Board	0·77	
Mahogany 2 in. + Felt	0·50	
Mahogany 2 in. + Blanket	0·66	
Mahogany 2 in. + Eelgrass Quilt, loosely fastened	0·34	

TABLE II.

Sound-transmission through Hair-felt.

Thickness per layer = 0·58 in.

Frequency.	Mean Transmission Ratio.			
	1 layer.	2 layers.	3 layers.	4 layers.
250	·242	·110	·0534	·0357
400	·232	·0949	·0420	·0210
500	·251	·0888	·0408	·0142
700	·221	·0740	·0222	·0086
1000	·233	·0676	·0185	·0050
1600	·261	·0595	·0098	·0022

It will be seen that these ratios also are, to a large extent, independent of the position of the point at which they were measured. Mean values of the amplitude ratios have been determined from the graphs given in figs. 6 and 7, and, by squaring these results, energy ratios have been calculated. These are given in Table I. (p. 189).

For the cases of reflexion from absorbent materials backed by the solid mahogany board, the complementary fraction $1-r$ probably corresponds to some extent with the Sabine coefficient of the surfaces of a room built of 2-inch mahogany panels and lined with the material in question.

The Transmission of Sound through various thicknesses of Hair-felt.

In order to investigate the effect of thickness on the transmission of sound through felt-like partitions, transmission ratios were determined for one, two, three, and four layers of felt.

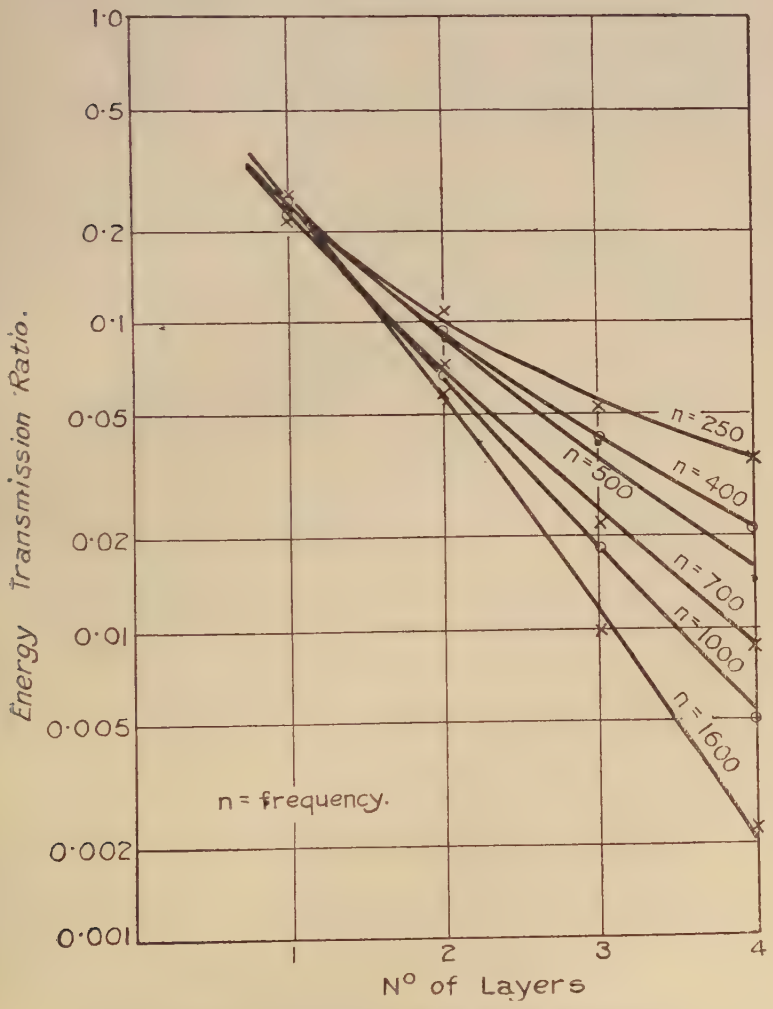
Observations were made at a number of frequencies, namely 250, 400, 500, 700, 1000, and 1600 vibrations per second. Owing to the low sensitivity of both source and microphone at the frequency of 250, they were fitted with horns to amplify the volume of sound and the sensitivity of the microphone respectively.

Transmission ratios were taken at the usual points along the transmitted beam. Results obtained were largely independent of the position at which they were measured. A mean energy transmission was obtained by squaring the mean amplitude ratio. Results are plotted as a family of curves in fig. 8, each curve showing for a given frequency the relation between transmission ratio and thickness of the partition. The smooth curves drawn, if continued, would all pass through the ordinate giving a transmission coefficient of unity at zero thickness of felt. It will be seen that the curves have but little curvature. Straight lines would indicate that each additional layer of felt reduces the transmitted sound in a constant ratio, and might be expected from materials which transmit sound only through pores. However, they would probably not be obtained from partitions which transmit any appreciable fraction of the incident sound through diaphragm-like vibrations. We have not attempted to obtain evidence of such diaphragm-like vibrations, but it is interesting that the late Prof. W. C. Sabine *

* W. C. Sabine, 'Collected Papers,' p. 99. Harvard Univ. Press, 1922.

found the absorbing power of felt applied to walls to be a maximum for certain frequencies, and was of the opinion that

Fig. 8.

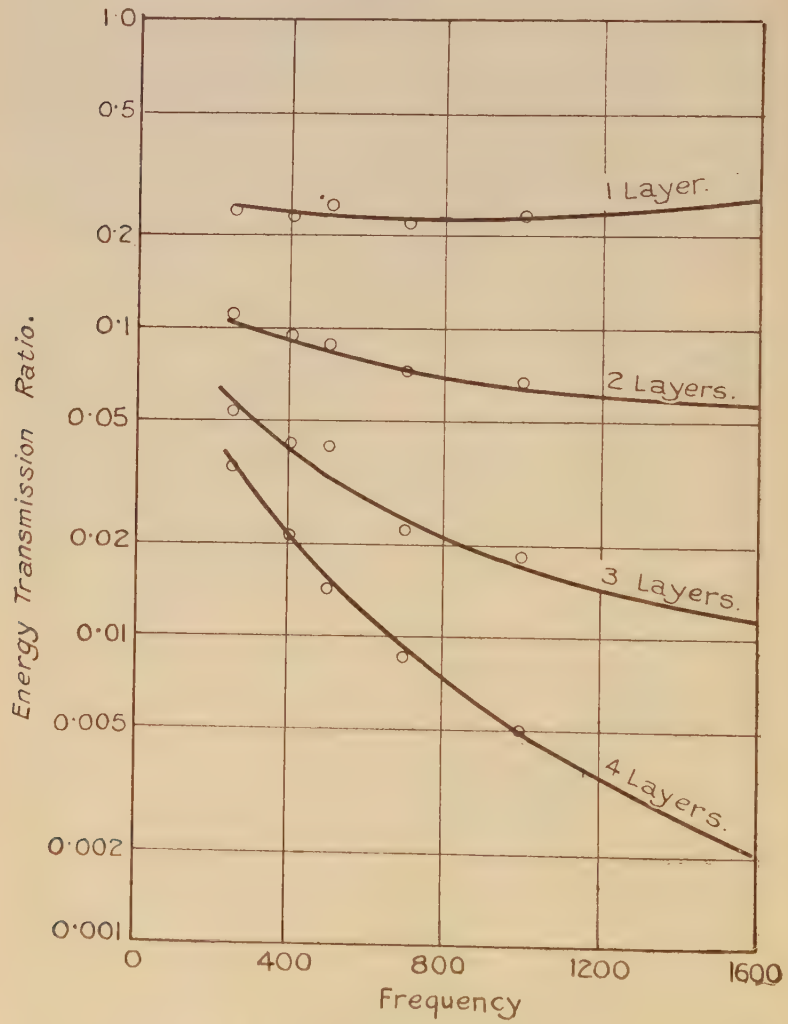


Sound-transmission through hair-felt at various frequencies.

the felt concerned absorbed sound partly by penetration of the sound into the pores, and partly through yielding of the mass as a whole.

In fig. 9 results are presented in an alternative manner, showing how the ratios vary with the frequency of the test note.

Fig. 9.

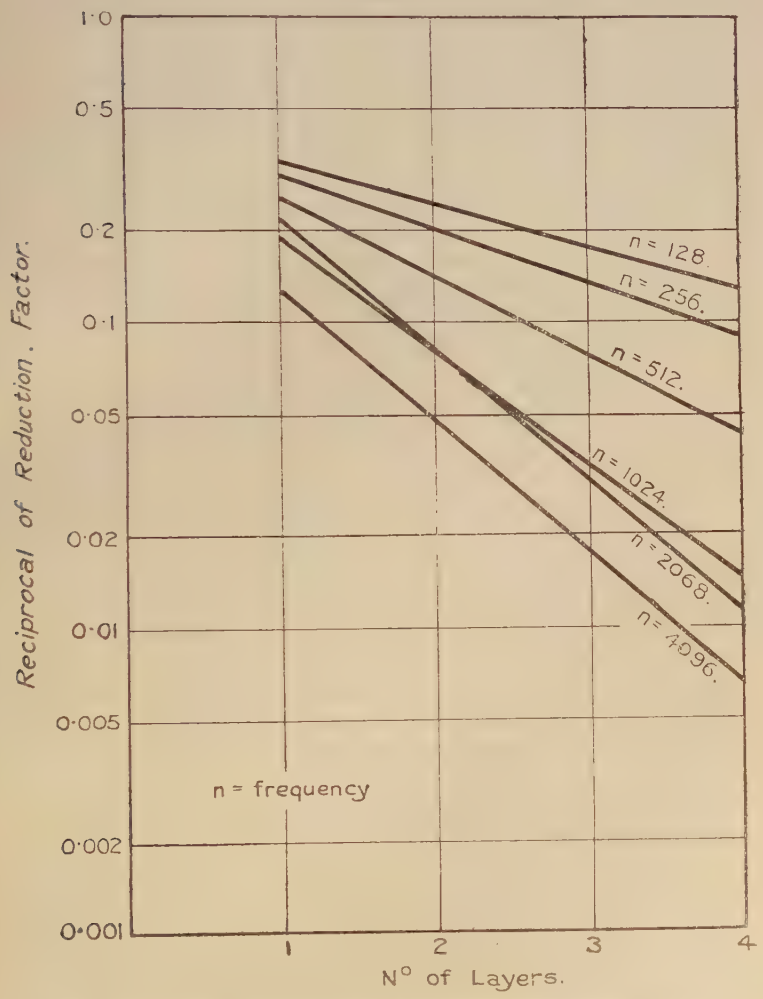


P. E. Sabine * investigated the transmission of sound through layers of hair-felt 3ft. × 7ft. in size by the reverberation method. The test panels were fastened over a doorway

* P. E. Sabine, 'American Architect,' Sept. 28, 1921.

between two rooms, in one of which was a source emitting sound. The duration of audible sound, after the source had

Fig. 10.



Sound-transmission through hair-felt at various frequencies (Sabine).

been stopped, was measured in both rooms. These measurements give the ratio of the intensities in the two rooms, a quantity which Sabine calls the Reduction Factor of the

Partition. While Sabine's reduction factor depends to some extent upon the acoustical conditions of the rooms as well as upon the coefficient of transmission of the partition, there is, nevertheless, a correspondence between the reciprocal of the Sabine's Reduction Factor and the transmission ratio as obtained by the present method. The type of felt used by Sabine, however, had a density of 9 lb. per cubic ft., while that used in the present method had a density of 12 lb. per cubic ft., but it is of interest to compare the results obtained by the two methods. In fig. 10 the reciprocal of the Reduction Factor as obtained by Sabine has been plotted against the thickness of the material, each layer being 1 inch thick. These curves are generally similar to those of the present experiments in that they give lines of little or no curvature directed towards a value of the neighbourhood of unity for zero thickness, and in particular the steepness of the curves increases in each case with increase of frequency. The chief difference is that, while Sabine's curves are all straight lines, they do not pass through the value unity when produced ; and while the curves of the present experiment would pass through the value unity, they are not quite straight.

Sabine suggests that surface phenomena in transmission by felt may explain why his curves do not pass through the value unity ; but it appears upon analysis * that, apart from such a cause, such divergences might arise in reverberation experiments from the conditions of the experiment.

The authors desire to acknowledge their indebtedness to Dr. G. W. C. Kaye, Superintendent of the Physics Department, who assisted in designing the sound-proof chambers. It is desired to thank him also for encouraging help and support. Mr. W. J. B. Elliott, Junior Observer, assisted with many of the observations.

September 1926.

*. Phil. Mag. vol. 1. p. 75 (1925).

XVI. *On the Reflecting Power of the Carbon Atom for High-frequency Rays.* *By* M. Ponte, *Agrégé de l'Université (International Education Board Fellow)* *.

Summary.

(1) In order to eliminate as far as possible the difficulties inherent in the question of the intensity of X-ray reflexion from crystals, diamond powder has been investigated by the method of the ionization chamber. The structure factor $1/\sqrt{2}$ has thus been found for the amplitude, and a law of variation with θ is given for the reflecting power, which is the same for several wave-lengths.

(2) In comparing the energies reflected from the powder of diamond and the powder of rock-salt, for which the quantity $f_{Na}+f_{Cl}$ is given by W. L. Bragg's experiments (found suitable for powders), it has been found that $f_{C_{(111)}}=2{\cdot}7_5$ to about 10 per cent. accuracy $\left(\mathrm{S}f_{(111)}=\dfrac{2{\cdot}7}{\sqrt{2}}=1{\cdot}9_5\right)$.

(3) The same method, applied to the molecules of naphthalene and anthracene in Sir W. H. Bragg's models, gives for the reflecting powers of these molecules (cleavage planes) $\mathrm{F_N}=16{\cdot}5$, $\mathrm{F_A}=20{\cdot}2$ (temperature factor included in these figures). These values lead to $f_C=5{\cdot}7$ and $5{\cdot}9$ respectively. [It may be pointed out that in the limiting case of no deviation—which would correspond for all wave-lengths to an infinite spacing—the value of f_C should be the number of electrons in the atom, viz. 6. The spacing of diamond (111) is 2·05, of the cleavage plane in naphthalene 7·3, and in anthracene 9·15.] Graphite (cleavage) gave $f_C=3{\cdot}4$.

THE determination of the reflecting power of an atom for a high-frequency radiation, and its variation with the angle of scattering, is of the greatest importance for the investigation of the laws of scattering of an electromagnetic wave by the bound electrons of this atom and for the determination of the distribution of these electrons in the various shells. We may estimate this quantity by measuring the intensity of X-ray reflexion from the various planes of a crystal[1]; but at once we meet with difficulties, which arise generally from the fact that most crystals seem to be formed of small perfect blocks, of which corresponding

* Communicated by Prof. W. H. Bragg, K.B.E., F.R.S.

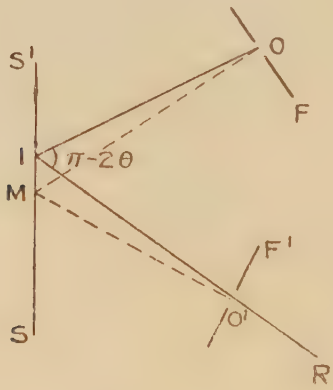
planes are orientated only approximately parallel. The intensity of reflexion depends on the deviation of the blocks from parallelism and on their magnitude (primary extinction) [1]. Not only are these quantities unknown, but also they are certainly not the same for the surface of the crystal and for the interior of its volume. The study of reflexion by powders offers the two following advantages: it is a means of reducing the primary extinction by decreasing as much as possible the sizes of the blocks—all the parts of the volume of the powder (great enough for all directions to be equally probable) are equivalent.

The first step towards finding the laws of scattering by atoms is to study the reflected intensity from powders of single elements. We have commenced with carbon, as diamond, using the ionization method.

Experimental Arrangement.

This is described in 'X-Rays and Crystal Structure,' p. 25. In order to have a sufficient reflected intensity, we are led to

Fig. 1.

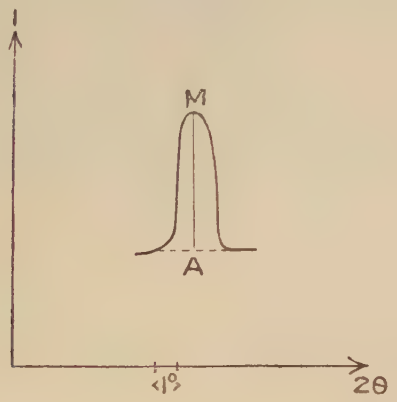


bathe the whole surface SS' of a powder by an X-ray beam coming from O (fig. 1). If, now, SS' is a plane and $OMS' = O'MS = \theta$ [O', slit of the chamber] with $OM = O'M$, the reflected rays are focussed near to O', and the powder can be set on an ordinary spectrometer of which O is the slit, parallel to the plane of the powder. At O' we obtain an "image" of the slit, the characteristics of which it is not profitable to discuss here [2]. For $\theta < 45°$, for instance, it has a sharp edge on the side of decreasing spacings. For a surface SS' it is

more diffuse on the other side, and, the powder having a certain thickness, the image will spread off still more on this side, the effect being greater for less absorbing powders and small values of θ. The difficulty is overcome if care is taken to have a slit O′ large enough to receive all the image, and to avoid overlapping images. When necessary (small θ, for instance) to suppress any trouble coming from the K_β images, K_β is absorbed by filters—for Mo by ·04 cm. of zirconium oxide and for Cu by ·0025 cm. of Ni.

The method of measuring the reflected energy for a given spacing consists in leaving the powder fixed at the angle θ and rotating the chamber fitted with a slit F′ large enough

Fig. 2.



to take in all the image. We obtain a curve such as is represented in fig. 2; the two external parts give the white radiation effect (they are generally at the same height). MA is the quantity required; F′ must be taken as narrow as possible, for the effect of the white radiation is exaggerated with this arrangement, because the angle between two lines which join any point of the powder with two points of F and F′ respectively gives a reflexion of several wave-lengths (each spacing gives at least one, within the excitation limits of the tube). The chamber of the spectrometer used had no vernier; the conditions were thus not favourable (generally slit F′ was 2–3 mm., for F 0·8 mm.), and in the strongest reflexions the maximum did not exceed five times the effect of the white radiation.

The powder was mounted in the following manner:—On a support S (fig. 3) pierced with an aperture O were pasted a piece of cellophane (·5 mm.), then two glass plates which formed a cavity of known thickness s (1–1·6 mm.), in which is pressed the powder. No kind of glue or paste was used; if necessary, the powder was covered with a very thin cellophane leaf (·01 mm.) to support it. By keeping the surface of the glass clean and pressing the powder with a flat plate, it is possible by this means to obtain a thickness of powder which is known to ·02 or ·03 mm.

Fig. 3.

The tube used was a Shearer tube, actuated by a transformer. It is difficult to maintain the tube quite steady, and as a consequence the accuracy of the measurements is not great (*cf.* below). The divergence of the X-ray beam was varied from less than 1° (small values of θ) to 4° for large values of θ.

Theory: Formulæ.

If E is the reflected energy, the same theory as W. L. Bragg's for a crystal [3]—but here it is useless to rotate the powder, since each incident ray is used in the same way: E replaces Eω—shows that

$$\frac{E}{I} = \frac{1}{2\mu} \cdot (1 - e^{-2\mu s \sin\theta}) B. \quad . \quad . \quad . \quad . \quad (1)$$

B Δv is the factor which represents the reflexion from the volume Δv (B replaces Q). If A Δv is this factor for the whole of a reflected cone, $2a$ the height of the slit of the chamber, and D its distance from the centre,

$$B = A \cdot \frac{\arcsin(a/D \sin 2\theta)}{\pi} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The factor A has been given by Darwin [4]. We may calculate it from the formula which W. L. Bragg found for the reflexion from a small perfect crystal built up of m planes of spacing d, m being small enough *to avoid primary extinction*, which received an intensity i at an angle $\theta + u$:

$$dR = \frac{\sin\theta}{m} \cdot i' \cdot \frac{\sin^2 m\phi}{\sin^2 \phi} \cdot dV, \quad . \quad . \quad . \quad (3)$$

where $\phi = \frac{2\pi d \cos\theta}{\lambda} \cdot u$; i' is the energy reflected by one plane. If we consider a volume of powder ΔV sufficiently large for all directions in it to be equally probable (depth

small enough, however, to have negligible absorption), dv being the mean value of the powder-grains, there are $\frac{1}{2}\frac{\Delta V}{dv}\cos\theta\,.\,du$ elements, of which the normal makes the angle $\frac{\pi}{2}-(\theta+u)$ with the incident ray (u is taken small because the expression (3) has a strong maximum when $u=0$). If there are ν planes * of the same spacing d, the reflected energy for this spacing d will be

$$E_{\Delta\nu}=\nu\frac{\lambda\sin\theta}{4\pi md^2}\,.\,i'\Delta V\int\frac{\sin^2 m\phi}{\sin^2\phi}\,.\,d\phi=A\,.\,\Delta V.$$

Replacing i' by its classical value, and taking the integral from $-\pi/2$ to $+\pi/2$, since u is very small, we have

$$A=\frac{\nu}{4}\,.\,\frac{1+\cos^2 2\theta}{\sin\theta}\,.\,e^{-B\sin^2\theta}\,.\,\lambda^3\,.\,N^2\,.\,S^2\,.\,f^2(2\theta\,.\,d,\text{ face})\,.\,\epsilon^2. \quad (4)$$

[N, number of scattering atoms per cm.^{3} ;
ϵ, reflecting power of an electron for a direction which is perpendicular to the field (e^2/mc^2) ;
$f\epsilon$, the reflecting power for the atom studied ;
S, geometrical structure factor.]

a/D is of the order 1/13 : for the values of θ studied arc sin and sin are the same, and, calling

$$\phi(\theta)=\frac{1}{\sin 2\theta}\,.\,\frac{1+\cos^2 2\theta}{4\sin\theta}\,.\,e^{-B\sin^2\theta}\,.\,\epsilon^2, \quad . \quad . \quad (5)$$

we find

$$\frac{E}{I}=\nu\,.\,\frac{a}{\pi D}\,.\,\phi(\theta)\,.\,\frac{1}{2\mu}(1-e^{-2\mu s\sin\theta})\lambda^3\,.\,N^2\,.\,S^2f'^2, \quad . \quad (6)$$

which is the formula used here.

Rock-salt †.

It was interesting to see what result was to be found for rock-salt, since W. L. Bragg's experiments [3] are subject to the criticism that, if the salt is not ideally perfect, primary extinction occurs, and this fact is not allowed for. Moreover, we have used the CuK_α radiation ; the temperature factor, depending only on $\sin\theta/\lambda$, has been taken to be the same as

* A centre must always be added to the elements of symmetry if it is not present.

† During the preparation of this paper appeared the paper of Havighurst, which leads to the same conclusions.

for Rh. The salt was crushed for a long time ; the grains were of the order 0·1–·005 mm. ; $e^{-2\mu s/\sin\theta}$ is zero ; and we have for two spacings at angles θ_1, θ_2 :

$$\frac{E_2}{E_1}=\frac{\nu_2}{\nu_1}\frac{\phi(\theta_2)}{\phi(\theta_1)}\cdot\frac{S_2^2 f_2^2}{S_1^2 f_1^2}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

E_2/E_1 is accurate to 10 per cent. ; this gives f_2/f_1 to 5 per cent. The following results were obtained :—

Planes.	Ratios f/f_{100}. Obs.	W. L. Bragg.
(110) $(f_{Na}+f_{Cl})$	0·81	0·8
(222) („)	0·69	0·67
(210) („)	0·53	0·54
(111) $(f_{Cl}-f_{Na})$	0·22	0·208

(111) is very weak, which explains the greater difference found for this plane.

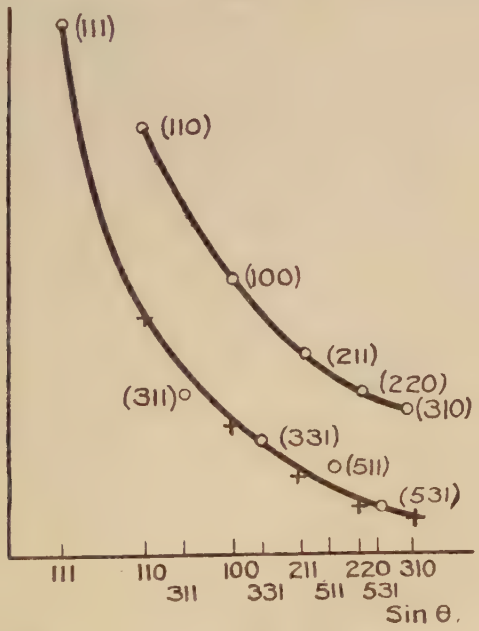
The purpose of this work was not the study of rock-salt, and the comparison has not been pushed further ; it shows sufficiently well that the results are the same, which is in agreement with the last paper of W. L. Bragg, Darwin, and James [1], who show that rock-salt approximates to the ideally imperfect state ; at least, the size of the blocks which form a crystal of rock-salt is something smaller than ·01 or ·005 mm. Moreover, the law of variation of f is the same for K_α Cu and K_α Rh : it depends only on $\sin\theta/\lambda$, which is to be expected, since we are far enough from the K level of Cl. We may therefore assume, too, that the absolute values of f are the same, for a given spacing, as those given by W. L. Bragg.

Diamond.

The powder was formed of very fine grains (most of them being between ·005 and ·002 mm.) interspersed with a few larger blocks (·02 mm.), which were sufficiently large to give distinct spots on a photograph. The investigation was carried out for four wave-lengths—K_α Mo (0·708), K_αCu (1·537), K_β Fe (1·746), K_α Fe (1·931). To formula (7) are to be added the terms in $e^{-2\mu s/\sin\theta}$ only for K_α Mo, where $e^{\mu s}=1{\cdot}46$ ($s=1{\cdot}41$ mm.).

Because of the structure of diamond, the powers Sf calculated (without any temperature factor, since its effect is negligible in diamond[8]) must lie on two curves as functions of θ, the atoms being in phase for the planes which have at least one even index and in quadrature for the planes with all three indices odd. If all primary extinction is eliminated, the ordinates of the two curves should be in the ratio $1/\sqrt{2}$: if primary extinction does occur, the ratio should be greater and the limit—perfect crystal—is $1/\sqrt{2}$ for the *intensities*, and not for the amplitudes[5]. In this investigation it has been found clearly to be $1/\sqrt{2}$ for the amplitudes, as shown

Curve I.



by the curves I for K_α Mo and K_α Cu (abscissæ, $\sin\theta$); the circles are the values of Sf as calculated by the formulæ (6), (7); the crosses represent the ordinates of the upper curve divided by $\sqrt{2}$: they lie on the lower curve.

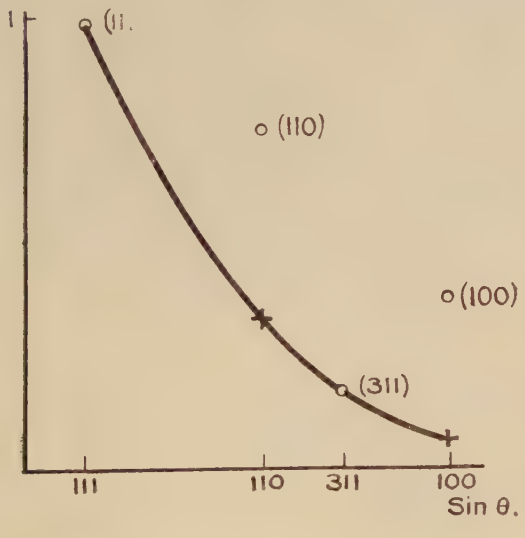
Allowance being made for this structure factor $1\sqrt{2}$ for the planes with three odd indices, the reflecting powers relatively to $f_{(111)}$ are [to 5 per cent. for the first planes, up to (100) inclusive, and 10 per cent. for the others which have been measured with respect to (100)] as shown in table, p. 202.

Planes (number divided by 2).	K_α Mo.			K_α Cu.			K_β Fe.			K_α Fe.		
	2θ.	P.	$f/f_{(111)}$.	2θ.	P.	$f/f_{(111)}$.	2θ.	P.	$f/f_{(111)}$.	2θ.	P.	$f/f_{(111)}$.
111 ... (4)	19° 50′	100	1	43° 50′	100	1	50° 30′	100	1	56° 10′	100	1
110 ... (6)	32° 30′	38·7	0·61	75°	31·5	0·6	88°	29·6	0·59	100°	34·6	0·6
311 ... (12)	38° 30′	10·6	0·51	91° 30′	8·5	0·5	108° 20′	11·1	0·52			
100 ... (3)	46° 50′	12·7	0·47	117° 20′	13·5	0·44						
331 ... (12)	51° 20′	4·9	0·45									
211 ... (12)	58° 10′	6	0·4									
$\left\{\begin{matrix}511\\333\end{matrix}\right\}$... (16)	62° 20′	3	$0·42_5$	—	—	—	$P=\frac{E}{\nu}\sin 2\theta.$					
220 ... (6)	68° 20′	3·6	0·36	—	—	—	$P_{111}=100.$					
531 ... (24)	71° 40′	$1·5_4$	0·36	(222) could not be found (too weak).								
310 ... (12)	78°		2·6	0·35								

The Table shows that, within the accuracy of the experiments, the law of variation is the same for the four wavelengths; it depends only on the spacing. Curve II., where the abscissæ represent $1/d$, shows this law of variation.

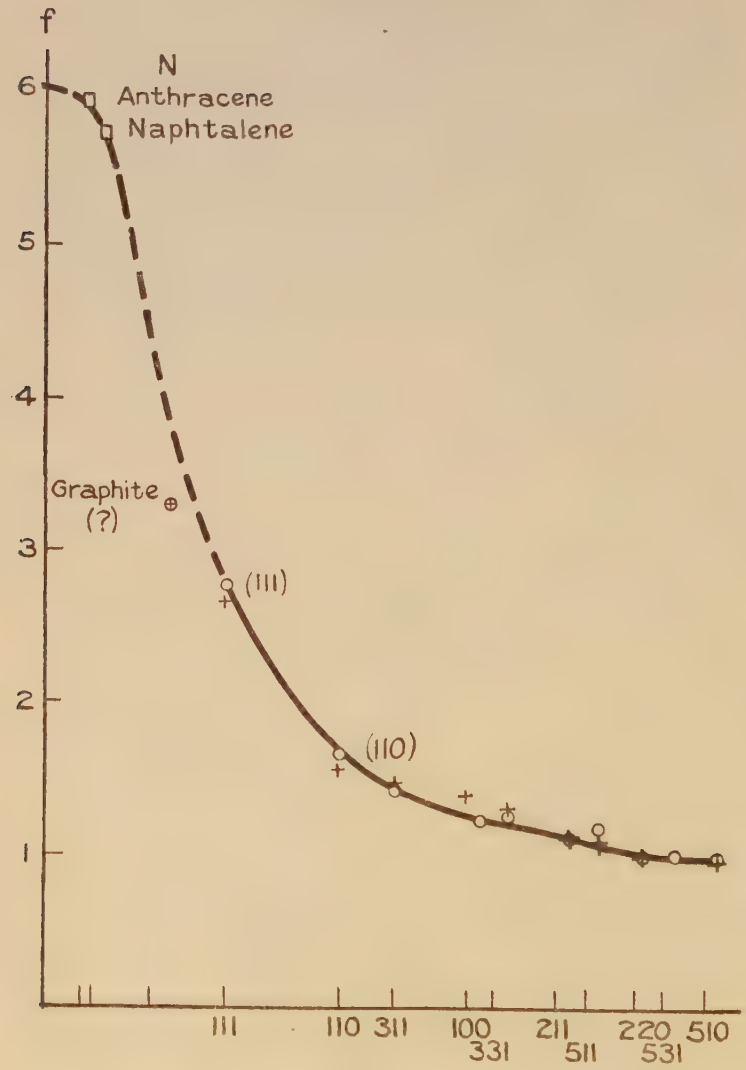
It was to be expected that this curve would not be a regular one. It is very unlikely that we may consider the average distribution of the electrons around the nucleus as having a spherical symmetry; the weak reflexion (222) must be explained in this way, and the electrons must

Curve II.



certainly participate in the symmetry of the crystal in their sharing with the four neighbouring atoms. Therefore f depends not only on θ, but also on the particular face under examination [6]. But here the observed irregularities cannot be ascribed to this effect, the accuracy not being sufficient. Even if the accuracy had been great enough, it would still be necessary to be sure, in working with powders of various sizes, that they are not caused by accidental variations from perfectly random distribution. We have had only one powder sample. We shall therefore assume, for the moment, that the curve is a regular one.

Curve III.



"Absolute" Measurements.

We must try now to evaluate $f_{(111)}$. We cannot hope to make a good absolute measurement, in the true significance of the word, with the arrangement used. But, if we may

consider the reflecting power $f'_{Na}+f'_{Cl}$ as known for rock-salt, it is sufficient to compare the reflected energies, for the same incident energy, from a powder of diamond and a powder of rock-salt, for given spacings. Formula (6) gives in this case :

$$\frac{E_D}{E_{NaCl}}=\frac{\mu_{NaCl}}{\mu_D}\cdot\frac{1-e^{-2\mu_D S_D \sin\theta_D}}{1-e^{-2\mu_N S_N \sin\theta_N}}\cdot\frac{\phi(\theta_D)}{\phi(\theta_N)}\cdot N_D^2\cdot S_D^2\cdot f_D^2, \quad (8)$$

where all quantities are known except f'_D. We may therefore calculate f_D. Comparison has been made for K_αMo between (110) Diamond and (110) NaCl. The absorptions were

$\mu=2{\cdot}9$ for diamond,

$\mu=9{\cdot}8$ for rock-salt powder ($s=1{\cdot}3$, about)

to 5 per cent. The mean value of the determinations gives $E_{D(110)}/E_{NaCl\ 110}=0{\cdot}85$ to 6 or 7 per cent. : f_D/f_N is therefore measured with an error not more than 10 per cent. The temperature factor for rock-salt—taken equal to that with Rh rays—is 0·91 (intensities); $1-e^{-2\mu s/\sin\theta}$ has the value 0·96 for diamond ($s=1{\cdot}6$) and 1 for rock-salt. We see therefore that $\left[N_D=\frac{1}{3{\cdot}564}A^{-3}\,;\ N_{Na+Cl}=1/2\times 22{\cdot}21\ A^{-3}\right]$:

$$f_{D(110)}=(f_{Na}+f_{Cl})_{(110)}\times 0{\cdot}10_2.$$

W. L. Bragg gives [3] $(f_{Na}+f_{Cl})_{(110)}=16{\cdot}2$; hence

$$f_{D(110)}=1{\cdot}65 \text{ and } f_{D(111)}=3{\cdot}7_5\ *.$$

* Measurements have been made, too, for K_αCu and K_αFe : the absorptions of the powder of diamond are $\mu_{Cu}=21{\cdot}2$; $\mu_{Fe}=24{\cdot}5$. They present therefore an anomaly which is certainly due to the presence of iron (oxide), of which the K limit is between K_αCu and K_αFe (the diamond has a greyish colour, which may be due to it). It is easy to measure this proportion of iron by means of these absorption-coefficients, for μ is a linear function of the quantities per cm.^{3} of carbon and iron and of the corresponding values of μ/ρ. If the calculation is made $\left[\left(\frac{\mu}{\rho}\right)_C=4_{(Cu)} \text{ and } 7{\cdot}62_{(Fe)}\,;\ \left(\frac{\mu}{\rho}\right)_{Fe}=268_{(Cu)} \text{ and } 66_{(Fe)}\right]$, we find $m_{Fe}=0{\cdot}035$ gr. and $m_C=2{\cdot}91$. The coefficient μ calculated from Mo from these values is 2·84 ; it was found to be 2·9. There is, therefore, little doubt that we have a small quantity of iron in the powder. It is not sufficient to invalidate the value of $f_{(111)}$ which has been found ; in formula (6), for an impure diamond, we must take the volume concentration of the diamond : according to the numbers given here, there is at the most ·01 cm.^{3} of impurity by cm.^{3} of powder.

The absorption for NaCl could not be determined in a suitable way : it is too great, and we must take so small a thickness of powder that the

Carbon has 6 electrons; f_0 should be 6. The reflecting power for Diamond (111) is therefore already fallen off to less than half its value (effective value for the reflexion by this plane $2{\cdot}75/\sqrt{2}=1{\cdot}95$).

We tried to estimate the reflecting power of the carbon atom nearer to $\theta=0$ by examining two hydrocarbons of which the structure is approximately known—naphthalene and anthracene. The method has been applied to the cleavage plane (first order) with K_α Cu. It was not possible to obtain a good naphthalene powder: after long crushing there are still flakes as large as 0·1 mm., and the results are doubtful. But the powder of anthracene (a commercial powder) was a very good one, the grains of which were for the most part between ·005 and ·002 mm.; the largest grains, of which there were very few, did not exceed ·015 mm. The results are as follows:—

	N.	2θ.	μ.	$E/E_{D_{(111)}}$.	$F/f_{(111)}$.	F.
Naphthalene...	$2/368\ A^{-3}$	12°	2·35	2·4	6	16·5
Anthracene ...	$2/474\ A^{-3}$	9° 50′	3·7	$2{\cdot}0_5$	$7{\cdot}3_5$	20·2

where F is the reflecting power of the molecules.

If, now, we adopt the models proposed by Sir W. H. Bragg, we may calculate the geometrical structure factor of these molecules for the cleavage plane. If we may consider that the total wave emitted from one of the constituent atoms has the phase which corresponds to its centre—which is only an assumption, giving to the average distribution of the electrons a centre of symmetry on a plane of symmetry parallel to the cleavage plane—the total scattered wave will be

$$f_{C_{2\theta}} \times S_C + f_{H_{2\theta}} \cdot S_{H_{2\theta}} = F,$$

accuracy is absolutely without any value. It has been calculated by the λ^3 law from 9·8 for K_α Mo. It gives $\mu_{Cu}=100$; $\mu_{Fe}=200$. The comparison $D_{(111)}$ and $NaCl_{(110)}$ for K_α Cu gives

$$E_{C_{(111)}}/E_{NaCl_{(110)}}=3; \quad \text{hence } f_{C_{(111)}}=2{\cdot}6_2.$$

The comparison $C_{(111)}$ and $NaCl_{(100)}$ for K_α Fe:

$$E_{C_{(111)}}/E_{NaCl_{(100)}}=2{\cdot}7; \quad \text{hence } f_{C_{(111)}}=2{\cdot}6 \ (56).$$

These values are in good agreement with that found for K_α Mo, but the calculation of μ for the salt makes them debatable, and we must accept them with reserve.

where S_C and S_H are the geometrical structure factors for the centres of the atoms. We know that, for instance,

$$S_C = | \Sigma_1 e^{i2\pi d/\delta} | \quad \text{(first order)},$$

where d are the distances from the centres of the atoms to the cleavage plane, and δ the spacing belonging to this plane. In Sir W. H. Bragg's models :

Naphthalene, $C_{10}H_8$. $\left\{ \begin{array}{l} d :— \text{C} : \pm 0{\cdot}28,\ \pm 0{\cdot}4,\ \pm 1{\cdot}68,\ \pm 1{\cdot}81,\ \pm 2{\cdot}12; \\ \text{H} : \pm 0{\cdot}32,\ \pm 1{\cdot}72,\ \pm 2{\cdot}84,\ \pm 3{\cdot}56; \ \delta = 7{\cdot}3. \end{array} \right.$

Anthracene, $C_{14}H_{10}$. $\left\{ \begin{array}{l} d :— \text{C} : 0{\cdot}61,\ \pm 0{\cdot}81,\ 1{\cdot}18,\ \pm 1{\cdot}4,\ \pm 2{\cdot}6,\ \pm 2{\cdot}8, \\ \pm 3{\cdot}4\ ; \ \text{H} : \pm 0{\cdot}68,\ \pm 1{\cdot}29,\ \pm 2{\cdot}7,\ \pm 3{\cdot}7, \\ \pm 4{\cdot}5\ ; \ \delta = 9{\cdot}15. \end{array} \right.$

The calculations with these numbers give

$$F_N = 3{\cdot}1 f_{C_{12}} - 1{\cdot}43 f_{H_{12}},$$

$$F_A = 3{\cdot}56 f_{C_{9{\cdot}50}} - 1{\cdot}12 f_{H_{9{\cdot}50}}.$$

According to Hartree's calculations, $f_H = 0{\cdot}97$. Replacing F_N and F_A by the values found, we have

$$f_{C_{12}} = 5{\cdot}7_5,$$

$$f_{C_{9{\cdot}50}} = 5{\cdot}9_5.$$

The accuracy of the measurements does not exceed 10 per cent. : such an agreement is therefore probably an accidental one (moreover, there is a small unknown correction for the temperature factor). However we may consider that they are in favour of the method and the models given by Sir W. H. Bragg.

Finally, a few measurements have been made with graphite. We give the result, although it is uncertain : the powder, if pressed too strongly, orientates itself along the cleavage plane, and this falsifies the measurements. The powder (grains ·01 mm.) was very slightly pressed, and the cleavage (first order) compared with $C_{(111)}$ for K_α Cu and K_α Fe ($\mu_{Cu} = 4{\cdot}8$; $\mu_{Fe} = 8{\cdot}5$). It gave for Cu $f_{(00{\cdot}2)} = 3{\cdot}5$ and $f_{(00{\cdot}2)} = 3{\cdot}3$; the mean value is 3·4. If the result is not invalidated by possible orientation of the powder, it shows that f_C must decrease still more abruptly—at least in the beginning—for graphite than for diamond. This agrees with the structure of graphite.

Discussion.

We must see if the value 2·7 for $f_{C_{(111)}}$ is not too low because of primary extinction. Let us suppose a small perfect crystal, formed of m layers of reflecting power q. Darwin has shown that, calculating f for this crystal by the formulæ which assume no primary extinction, we find

$$f^2_{\text{calc.}} = f^2_{\text{real}} \cdot \frac{\tanh mq}{mq}.$$

Assume

$$f_{\text{real}} = 6\,;\ f_{\text{calc.}} = 2{\cdot}7\,:\ \frac{\tanh mq}{mq} = \frac{(2{\cdot}7)^2}{36} = 0{\cdot}2;\quad mq = 5 (\tanh mq = 1).$$

As $$q = 2 \cdot \frac{f}{\sqrt{2}} \mathrm{N}\, d^2e^2/mc^2 \text{ (usual notations)},$$

$$= 1{\cdot}5 \cdot 10^{-4},$$

and $$m = 3 \cdot 10^4 \text{ layers},$$

which gives a thickness of the block equal to $6 \cdot 10^{-3}$ mm., it is approximately the size of the grains of the powder used ; but, in this case, we should have $\tanh mq = 1$: the primary extinction would be strong enough for the structure factor to be $1/\sqrt{2}$ for the intensities and not for the amplitudes. We found $1/\sqrt{2}$ for these amplitudes; therefore it is not the primary extinction which is the cause of the fall in $f_{(111)}$; if it has modified it, it is only to a small degree (10 per cent. at most). It is to be explained by the fact that, although a few diamonds appear as nearly perfect, they, too, are generally imperfect, and the small blocks of the powder are not perfect crystals.

It is probably premature to draw conclusions about the distribution of electrons in the carbon atom. We cannot apply to crystals the results given by optical measurements from spectra for the sizes of the orbits because the conditions of existence for the atom are quite different in the two cases. We must take the converse problem and deduce these orbits from the law of $f(\theta)$. For this purpose we have, up to the present, only Hartree's calculations [7], which are subject to many criticisms (spherical distribution, free electrons, etc.). We shall be able to be more certain when we have collected a great number of the functions ($f(\theta)$) for the atoms of the elements. If, however, we try to obtain the sizes of the orbits of the carbon atom as given by Hartree's calculations [7], we see that the most important feature is the impossibility

of obtaining agreement with four identical L electrons. The best agreement (it is perhaps not the only one) is given by two K electrons on circular orbit with $r=0{\cdot}2$ A.U., one L electron on a circular orbit ($r=0{\cdot}7$ A.U.), and three on elliptical orbits (major axis 1·23 A.U.). It is probably the sizes of these orbits which are open to criticism.

I wish to express my sincere thanks to Sir W. H. Bragg for his helpful advice, to the Managers of the Davy-Faraday Laboratory for affording me facilities for carrying out the work, and to the International Education Board for the grant of a fellowship. Sir Charles Parsons very kindly obtained for me the diamond powder.

July 15th, 1926.

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XVII. *On the Electric Field near the Surface of the Atoms of Certain Elements as deduced from the Doublet Separations of their Spectra.* *By* N. R. Sen, *D.Sc.**

THE explanation of the fine structure of spectral lines originates with Sommerfeld's application of relativity mechanics to Bohr's atomic structure, and his theory has yielded many beautiful results with regard to X-ray doublet separations and the fine structure of the spectra of hydrogen-like atoms. Mr. Landé † has extended the theory to the case of optical doublets and has given a formula for the doublet separations of optical spectra which, on the whole, is found to work satisfactorily. When the orbit of the radiating electron penetrates the core it is moving in

* Communicated by the Author.
† *Zeit. f. Phys.* vol. xxv. p. 46 (1924).

fields of widely different strengths at the perihelion and aphelion. Inside the core the field is stronger and the electron can be supposed to be under the influence of a comparatively large effective nuclear charge depending upon the degree of penetration, while far outside, where the outermost part of the orbit is situated, the field is weaker and is practically hydrogen-like. If Z_e and Z_a be these two effective charges inside and outside Landé gives the doublet separation of the corresponding orbits in the form

$$\Delta\nu=\gamma\,.\,\frac{R\alpha^2.Z_a^2\,Z_e^2}{n_e^3\,.\,k\,.\,k'},$$

where $$\gamma=1+\frac{5}{8}(\alpha Z_e)^2+\frac{53}{128}(\alpha Z_e)^4+\ldots.$$

is a higher relativity correction, α^2 the fine structure constant, R Rydberg constant, k, k' two azimuthal quantum numbers, and n_e the effective quantum number of the orbit.

The approximate effective quantum number for the orbits can be obtained from the formula

$$\nu=\frac{R\,.\,Z_a^2}{n_e^2}.$$

In these formulæ Z_a is put equal to 1 for the normal atom or 2, 3, ... according as the ionization of the atom is of the first, second, or higher order respectively. The substitution of the spectroscopic values of $\Delta\nu$ and ν in the above equations shows that within a sequence with a definite azimuthal quantum number k, Z_e is practically constant. The first member of the series has been found in some cases to provide exceptions. In an atom with three electrons on the outside shell this is much more pronounced, as the following table * shows :—

One-electron system (p doublets).

Li	0·94			
Na	7·5	7·7	7·7	
K	14·8	15·6	15·0	15·6
Rb	31·1	30·9	30·8	31·5
Cs	47·7	47·6	47·0	47·8

Three-electron system (p doublets).

Al	11·5	10·0	10·2	10·2
Ga	30·8	26·3	26·5	27·1
In	51·8	43·7	43·4	44·3
Tl	86·7	77·0	75·0	75·0

* The Table is taken from Landé's paper.

A glance at the first column of the second table will bear out the above remark. An explanation for this can, however, be easily obtained *. The above figures are all calculated on the assumption $Z_a = 1$. The radiating electron, even when moving outside the core, is in a complicated field which is surely not hydrogen-like with unit nuclear charge. It is only in the case of the orbits of the higher members of the sequence which have their aphelia lying far outside the surface of the atom that Z_a can be taken to be unity, and consequently the constancy in the value of Z_e begins to be marked only with such orbits.

Let us suppose that such is really the case and try to arrive at some quantitative results from this. The field is always supposed to be central, and we can consequently take the charge anywhere to be a function of the distance of the point from the centre of the core. Consider the case of Al. It has got two electrons in 3_1 orbits loosely bound to the core and the series electron in a 3_2 orbit. We shall suppose that the aphelion of this 3_2 orbit is not very far from the farthest part of a 3_1 orbit and is directly under its influence. We take the effective charge at this distance to be C. The orbit near the aphelion is under the influence of an effective charge C and at the innermost part of the core of a charge Z_e, hence the doublet separation for the orbit is given by

$$\Delta\nu = \gamma \cdot \frac{R\alpha^2 C^2 Z_e^2}{n_e^3 \cdot k \cdot k'} \cdot \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The effective quantum number n_e we take to be given by the usual formula

$$\nu = \frac{RC^2}{n_e^2} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We have here supposed the outermost part of the orbit to be in a hydrogen-like Coulomb's field with effective charge C. The above relation is obtained by comparing the actual orbit with such a fictitious orbit of equal energy. For p orbits we take $k = 2, k' = 1$. Now the effective nuclear charge Z_e depends upon the degree of penetration, which again depends primarily on the azimuthal quantum number k. Hence we shall not be far from right if we take Z_e to be approximately constant for the entire sequence. The choice of this constant value is to be made by examining the values for the subsequent members of the sequence. The first value where this approximate constancy is attained can

* A. Landé, *l. c.*; also D. Hartree, Proc. Camb. Phil. Soc. vols. xxii.–xxvi. p. 904 (1925).

be taken, or where there is some doubt between two successive values the mean can be accepted for calculation. Equations (1) and (2) then enable us to calculate n_e and C from the measured values of $\Delta\nu$ and ν. In Al, Ga, In, and Tl we have in each case two electrons outside in s orbits and the series electron in a p orbit. Since the surfaces of the atoms of these elements are similar in structure we should expect an almost uniform value of C in all these cases. Calculations really fulful this expectation, as will be apparent from the following table :—

	Z_e	n_e	C.
Al (13)	10·0	1·14	0·75
Ga (31)	26·2	1·09	0·72
In (49)	43 7	1·09	0·70
Tl (81)	75	1·08	0·70

(Higher relativity corrections are to be made in the last three cases.)

The values of C less than 1 appear to be unexpected. The defect from unity is considerable in each case, and only a small part of it can be due to the uncertainty in the value of Z_e. In this connexion we may recollect that the effective charge of the p orbit of Li is less than unity, being equal to 0·94. The p orbit of Li is non-penetrating, and the field near the perihelion may in this sense be roughly compared with the field at aphelia of the first p orbits of Al, Ga, etc. The comparison with the first p orbit of B would have been interesting, but the spectra of B have not as yet been classified. The large defect of the effective charge from unity suggests that the aphelion of the first p orbit is fairly close to the aphelion of the s orbit in which, say, one of the loosely-bound electrons moves, so that the repulsion between the electrons is an important factor in determining the resultant field there. Consequently it is also necessary to assume that both the electrons appear at the aphelia at approximately the same time, since this synchronism would produce the maximum repulsive effect. The main core charge certainly determines to a great extent the field at the aphelion of the first p orbit, but the loosely-bound electron must also be playing a very important part in this respect.

Mr. Landé has also applied his formula to the case of triplets ($mp_3 - mp_1$). The results are, however, less satisfactory than in the case of doublets. The first member shows, as before, some irregularity, but the effective charge does not in general fluctuate about some constant value, or at any rate it is difficult to find it. But in the case of Zn and Cd

triplets the constant Z_e can be easily chosen, and the results of calculation after making the higher relativity corrections are interesting.

	Z_e	n_e	C.
Zn (30)	24	1·16	0·73
Cd (48)	41·3	1·16	0·71

The values of n_e and C are approximately the same as in the case of Al, Ga, In, or Tl. Now the normal Zn and Cd atoms have got two electrons in 4_1 and 5_1 orbits. For p doublets one of these electrons must be supposed to be in the p orbits and the other in an s orbit. Hence in this case also the aphelion of the p orbit is under the influence of the *one* electron moving in the s orbit. It thus appears legitimate to conclude that as here the first p orbit in the case of Al or Ga etc. is influenced by only *one* of the two electrons moving in s orbits. The uniformity in the values of n_e and C is thus easily explained.

University College of Science,
Calcutta,
10th March 1926.

XVIII. *A Note on the Electric Potentials of Ions in Salt Solutions.* *By* J. A. V. Butler, *M.Sc., University College of Swansea* *.

IN Debye and Hückel's calculation † of the electrical forces between the ions in a salt solution, the first and fundamental step is the calculation of the potential ψ_i of an ion of the ith sort, due to the electric field of the ions about it. ψ_i is obtained as a function of the total ionic strength κ of the solution $\psi_i = -z_i\epsilon\kappa/D$.

In his second derivation ‡, Debye obtained the electrical free energy from this by the use of a fictitious charging process. Assuming the ions to be initially uncharged he calculated the electrical work required to increase the charges reversibly to their final values, in such a way that at a given instant all the ions have acquired the same fraction λ of their final charge. The total electric work required for this process, $A = \Sigma^1/_3 n_i\epsilon z_i\psi_i$ where z_i is the number of unit charges ϵ on ions of the ith kind, of which there are n, is

* Communicated by the Author.
† *Physikal. Zeits.* xxiv. p. 185 (1923).
‡ *Ibid.* xxv. p. 97 (1924).

taken to be the electrical free energy of the solution. From it the partial free energies, and therefore the activity coefficients, can be obtained by differentiation. Bjerrum has shown * that the general differential of A,

$$A_i = \partial A/\partial n_i = -\frac{\epsilon^2 z_i^2 \kappa}{2D},$$

can also be evaluated by considering the charging of a single ion of the ith kind by a similar process. If a charge is introduced into a salt solution (of fixed κ) and increased by infinitesimal amounts, the potential ψ_i at its surface due to the ion atmosphere resulting is $e_i\kappa/D$ when a total charge e_i has accumulated. The work done in introducing a charge $z_i\epsilon_i$ is

$$A_i = \int_0^{z_i\epsilon} \frac{e_i\kappa}{D}\,de = -\frac{z_i^2\epsilon^2\kappa}{2D}.$$

In this note it is desired to show that this quantity does in fact function as the free energy.

It should first be noted that ψ_i, the electric potential at the surface of the ion due to its ion atmosphere, differs from the electric potential of the ion itself. The former is the electric work done in bringing unit charge to the surface of the ion, through its ion "atmosphere"; the latter is the electric work done in bringing the ion itself from a standard position into the interior of the solution. It does not appear to be possible to make a direct calculation of this quantity, but it is evidently given indirectly by A_i above. Hence, if V be the potential of the ion itself,

$$A_i = \epsilon z_i V \quad \text{and} \quad V = -\frac{z_i\epsilon\kappa}{2D}.$$

Now the condition of equilibrium of an ion in two phases is

$$\mu' + aV' = \mu'' + aV'',$$

where μ', μ'' are the chemical potentials (or partial free energies) of the ion, V', V'' the electric potentials in the two phases. Consider a simple concentration cell "without transport," which measures the free energy of transfer of a binary electrolyte from one concentration C_1 to a second C_2. For clearness we will take the case of NaCl. The cell is a combination of two sodium-chlorine cells with the two

* *Zeits. phys. Chem.* cxix. p. 145 (1926).

solutions, coupled back to back :

Na	NaCl	Cl_2—Cl_2	NaCl	Na
	C_1		C_2	
μ_{Na+}	$\mu'_{Na+}+\mu'_{Cl-}$	μ_{Cl-}	$\mu''_{Na+}+\mu''_{Cl-}$	μ_{Na+}
V_1	$V'_{Na+}+V'_{Cl-}$	V_{11}	$V''_{Na+}+V''_{Cl-}$	V_{111}

The potentials in the different parts of the cell are as written. To make units consistent with those used hitherto, the unit of mass to which they refer is the mass of a single ion for each species The conditions of equilibrium at the junctions are :—

$$\begin{aligned}
\mu_{Na+} + a_1V_1 &= \mu'_{Na+} + a_1V'_{Na+},\\
\mu_{Cl-} + a_2V_{11} &= \mu'_{Cl-} + a_1V'_{Cl-},\\
\mu''_{Cl-} + a_2V''_{Cl-} &= \mu_{Cl-} + a_2V_{11},\\
\mu''_{Na+} + a_1V''_{Na+} &= \mu_{Na+} + a_1V_{111},
\end{aligned}$$

whence the electromotive force of the combination (V_1-V_{111}) is given by

$$\begin{aligned}
a_1(V_1-V_{111}) = {} & \mu'_{Na+} + \mu'_{Cl-} + a_1V'_{Na+} + a_2V'_{Cl-}\\
& - (\mu''_{Na+} + \mu''_{Cl-} + a_1V''_{Na+} + a_2V''_{Cl-}).
\end{aligned}$$

The effect of the passage of electricity is the transfer of one molecule of NaCl from the one solution to the other, and since the cell is reversible this also gives the free energy change of the same transfer.

If the second solution is infinitely dilute its electric terms disappear, and we are left with

$$\Delta F = \mu'_{NaCl}-\mu''_{NaCl}+a_1V'_{Na+}+a_2V'_{Cl-}.$$

The last two terms represent the effect of electric interionic forces, hence for each ion $\Delta F_e = aV'$ and generally $\Delta F_e = -\epsilon^2 z_i^2 \kappa/2D$.

It may be observed that a novel conception in the treatment of heterogeneous equilibrium is introduced here. It has been the custom to assign a definite electric potential to each homogeneous phase. Evidently in a salt solution each ion species has a potential of its own. But the potential difference between two phases has the same value for all ion species, and the potential of a phase may be defined with respect to a standard phase in terms of the potential differences at the boundaries separating them. The general conditions of equilibrium which have been obtained elsewhere * are therefore not affected.

* Proc. Roy. Soc. A, cxii. p. 129 (1926).

XIX. *Discontinuous Flow past an Aerofoil.*

By Seinen Yokota *.

In the Philosophical Magazine for May, 1921, W. B. Morton gives a solution for the discontinuous flow of liquid past a wedge. The method has a wider range of application than at first appears, and the general solution of the flow of liquid bounded by two plane laminæ placed arbitrarily may be obtained by a similar process.

The discontinuous flow past an aerofoil has been a hobby of the present author for fifteen years or more, and the problem now seems to be partly solved by the following application of the modified Morton's method for the case of an aerofoil of very long aspect ratio in a current of perfect liquid.

Our daily experience and experiments show clearly that vortices are set up by the motion of a solid in a fluid initially at rest, while in a perfect fluid they can never occur theoretically. The birth of vortices is thus only attributable to the viscous nature of the fluid.

The vortex theory applied to an aerofoil admits the creation of vortices in one part but assumes their persistence in the remaining part of the reasoning. In spite of this obvious anomaly the coincidence of theory and experiments is quite noteworthy.

Another method of attacking the problem is to start from the strict supposition of the existence of velocity potential and to correct the result for the effect of viscosity, as is done in shipbuilding calculations, or with the aid of the Grenzschicht theory.

The following is a procedure of approaching the problem from the latter point of view.

In the plane $z=x+iy$, where i is the imaginary unit, let DCB and GH be two plane laminæ past which a liquid flows at an incidence angle α. β is the angle between DCB and GH as shown. The corresponding figures in the planes $w=\phi+i\psi$, where w is the complex potential, $\frac{1}{w}$, $\zeta=\frac{dz}{dw}$. $\log\zeta$ and t require no further explanations, the unit of speed being the general velocity of flow.

We have

$$\log\zeta=\mathrm{A}\int\frac{t-a}{\sqrt{(t-d)(t-g)(t^2-1)}}dt+\mathrm{B}, \quad . \quad . \quad (1)$$

where d, g, and a are values of t corresponding to the

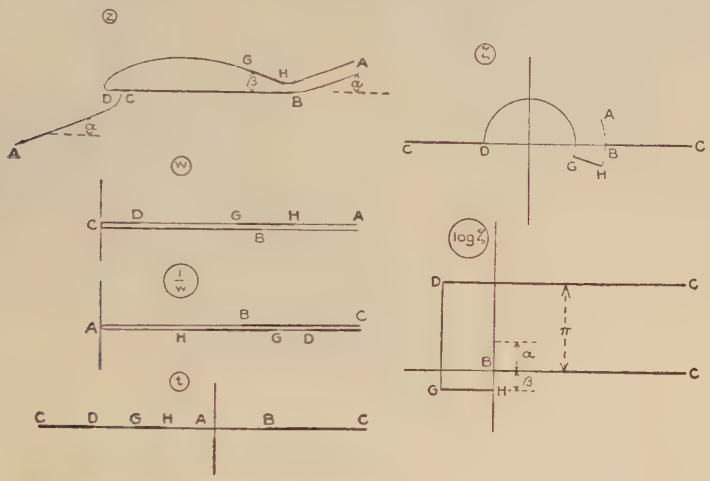
* Communicated by the Author.

points D, G, and A respectively. A and B are arbitrary constants.

$$w = \frac{C}{(t-a)^{\frac{1}{2}}}, \quad \ldots\ldots\ldots \quad (2)$$

where C is a real constant.

Fig. 1.



By the usual transformations

$$t = \frac{L+M\xi}{1+\xi}, \quad L+M = \frac{2(dg+1)}{d+g}, \quad LM = 1,$$

$$\left(\frac{M-D}{L-d}\right)^2 \xi^2 = \tau^2,$$

the expression under the sign of integration in the second member of (1) takes the normal form

$$\frac{t-a}{\sqrt{(t-d)(d-g)(t^2-1)}}dt = \frac{\sqrt{(L-d)(L^2-1)}}{i(Ld-1)\sqrt{g-L}}$$

$$\times \left[(M-a)\frac{d\tau}{\sqrt{(1-\tau^2)(1-k^2\tau^2)}} \right.$$

$$-(M-L)\frac{d\tau}{(1-L^2k^2\tau^2)\sqrt{(1-\tau^2)(1-k^2\tau^2)}}$$

$$\left. +(M-L)\frac{Lkd\tau^2}{2(1-L^2k^2\tau^2)\sqrt{(1-\tau^2)(1-k^2\tau^2)}} \right],$$

where $$k^2 = \frac{(L-d)^2}{(Ld-1)^2}.$$

Hence we get

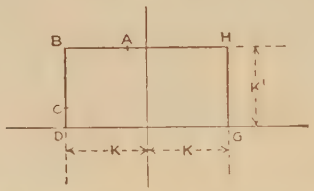
$$\log\zeta = C_2 u + C_1 \log\frac{H_1(l)H_1(u) - \Theta_1(l)\Theta_1(u)}{\Theta(0)\Theta(u+l)} + D, \quad (3)$$

where C_2, C_1, and D are constants and

$$\left.\begin{aligned} \frac{C_2}{C_1} &= \frac{i\sqrt{1-k^2L^2}}{\sqrt{L^2-1}}(L-a) + \frac{\Theta'(l)}{\Theta(l)}, \\ L &= \operatorname{sn} l, \qquad \tau = \operatorname{sn} u, \\ t &= \frac{L-k\tau}{1-Lk\tau}, \quad \tau = \frac{L-t}{k(1-Lt)}. \end{aligned}\right\} \quad (4)$$

The corresponding figure in the plane of the argument u is the parallelogram of periods as shown below (fig. 2).

Fig. 2.



With Schwarz and Christoffel representation, the inside of the parallelogram corresponds to the upper half of the t-plane.

Applying the boundary conditions, we find

$$C_2 = \frac{-i(\pi+\beta)}{2K}, \quad C_1 = 1, \quad D = -\log Q - \frac{i(\pi+\beta)}{2},$$

$$\log Q = \frac{1}{2K}\{\pi(K'-u_1) + K'\beta\}, \quad (5)$$

if $l = -K + iu_1$, and Q is the velocity of the liquid along the curved boundary DG.

From (4) and (5),

$$u_1 = \frac{1}{\pi}[K'(\pi+\beta) - 2K\log Q], \quad (6)$$

$$L = -\frac{1}{\sqrt{k}}\frac{H_1(iu_1)}{\Theta_1(iu_1)}, \quad (7)$$

$$a = L + \frac{\sqrt{L^2-1}}{\sqrt{1-k^2L^2}}\left\{\frac{\pi+\beta}{2K} + \frac{\Theta_1'(iu_1)}{i\Theta_1(iu_1)}\right\}. \quad (8)$$

At the point A, let $u_1 = iK' - u_2$ and $\tau = \tau_A$. Then

$$\tau_A = \frac{-1}{k\operatorname{sn} u_2},$$

and

$$-k\operatorname{sn} u_2 = \frac{k(1-La)}{L-a}. \quad (9)$$

The incidence angle α is given by

$$\alpha = -\frac{1}{2\mathrm{K}}(\pi+\beta)(\mathrm{K}-u_2) + \frac{1}{i}\log\frac{\mathrm{H}(iu_1)\Theta_1(u_2)-\Theta(iu_1)\mathrm{H}_1(u_2)}{\Theta(0)\mathrm{H}_1(u_2-iu_1)}. \quad . \quad (10)$$

The variable parameters in this problem are d, g, and a, but it is more convenient for practical purposes to take k, Q, and β as their substitutes.

The calculation of the argument u_2 from the relation (9) is directly effected by the author's formula

$$\cos\frac{\pi u_2}{\mathrm{K}} = \left(\frac{1}{2q}-q^3\right)\mathrm{B}+\frac{q}{2}\mathrm{B}^3+q^3\mathrm{B}^5, \quad . \quad . \quad (11)$$

where $$\mathrm{B}=\frac{\mathrm{dn}\,u_2-\sqrt{k'}}{\mathrm{dn}\,u_2+\sqrt{k'}} \text{ and } q=e^{-\frac{\pi\mathrm{K}'}{\mathrm{K}}}.$$

(See Journal of the Faculty of Engineering, Tokyo Imperial University, vol. xv. no. 2, May 1924.)

In the following, an example is given for the case of

$$k^2=\tfrac{1}{2}, \quad \mathrm{Q}=1{\cdot}2, \quad \beta=9^\circ.$$

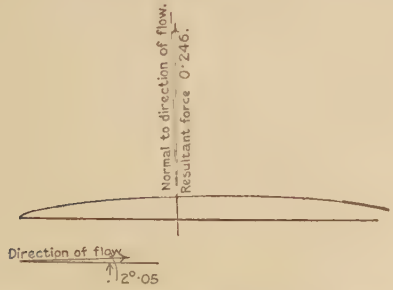
From this

$u_1=1{\cdot}732$, by (6) ;
$\mathrm{L}=-1{\cdot}407$, by (7) ;
$a=-0{\cdot}071$, by (8) ;
$u_2=1{\cdot}227$, by (9) and by my formula (11) ;
$\alpha=2^\circ{\cdot}05$, by (10).

To obtain the form of the aerofoil the values of ζ were plotted in terms of w and the integrations effected with an integraph.

The following figure (fig. 3) shows the form of the

Fig. 3.



aerofoil, the resultant force, the general direction of flow of liquid, and so on, the constant C in (2) and the density of liquid being both supposed unity. In this example the ratio of lift to drag is very high.

XX. *On the Thickness of the Optical Transition Layer in Liquid Surfaces.* *By* Prof. C. V. Raman, *F.R.S.*, *and* L. A. Ramdas, *M.A.*, *University of Calcutta* *.

1. Introduction.

In a series of papers contributed to the Proceedings of the Royal Society †, the authors have described their investigations on the scattering of light by clean and contaminated liquid surfaces which showed very clearly that even at ordinary temperatures and pressures a liquid surface is far from being a perfect optical plane, and that as the critical temperature is approached and the surface-tension diminishes, the increasing thermal agitation of the boundary becomes conspicuously evident by the brightening of the surface-opalescence. In the course of these researches, it occurred to the authors that it would be worth while to carry out a re-examination of the question whether the light reflected by a clean liquid surface at the Brewsterian angle is completely polarized or not. As is well-known, Jamin ‡ found that when light polarized at 45° to the plane of incidence is incident on a liquid surface at the Brewsterian angle, the reflected light is elliptically polarized; the coefficient of ellipticity K (which is the ratio of the amplitudes of the light-vector in and at right angles to the plane of incidence) was found by him to be negative for water and most aqueous solutions, and positive for many common liquids. The method used by Jamin for determining the ellipticity was not very well-adapted for such a delicate investigation, and apart from this, as was shown later by Lord Rayleigh §, his values for water and very probably also for aqueous solutions were vitiated by surface contaminations. For the cleanest water surfaces, Rayleigh found the ellipticity to have a small positive value 0·00042. The method employed by Rayleigh involves the use of sunlight and is very sensitive, being capable of determining ellipticities as small as 0·00010. The definitely positive value obtained by Rayleigh for clean water surfaces made it of interest to examine whether other liquids would also show an ellipticity of the same order of magnitude.

* Communicated by the Authors.

† C. V. Raman and L. A. Ramdas, Proc. Roy. Soc. A, vol. cviii. p. 561 (1925); vol. cix. pp. 150 and 272.

‡ For an account of the earlier work in this field, see Winkelmann's *Handbuch der Physik*, *Optik*, p. 1263 (1906).

§ Rayleigh, Scientific Papers, vol. iii. p. 496.

2. Measurements of the Coefficient of Ellipticity.

The work was taken up and the measurements were made during the summer of 1924 by one of us (L. A. Ramdas), the method of Rayleigh being used. No source of illumination other than brilliant sunlight was found to be sufficient. A heliostat reflected a beam of sunlight through an aperture into the dark room. This beam was reflected by an adjustable mirror at any required angle. The liquid was kept in a very thoroughly cleaned and dried dish with a piece of black glass at the bottom to give a good background. The dish was placed on a heavy table practically free from vibrations, and the light reflected by the surface of the liquid observed through a very good nicol rotating on a graduated circle provided with verniers reading to a minute. The angle of incidence was adjusted until a horizontal dark band was seen to cross the reflected image of the sun when the nicol was adjusted to cut off the reflected light. A quarter-wave plate of mica was then placed in front of the nicol and rotated in its own plane till the dark band was as distinct as before.

The incident light was then polarized by passing through a second nicol mounted on a graduated circle and adjusted so that its shorter diagonal made an angle of 30° with the plane of incidence. After taking the reading of the first nicol, the second nicol was turned through 60° so that the shorter diagonal made 30° on the other side and the first nicol was adjusted to get back the dark band again as distinctly as before. From the difference in the readings $\alpha' - \alpha$, the ellipticity K is determined, being equal to $\frac{1}{2}\tan 30°(\alpha' - \alpha)$ as shown by Rayleigh. A number of readings were taken for each liquid in the four positions of the quarter-wave plate at right angles to each other and K calculated from the mean value of $\alpha' - \alpha$.

For all the organic chemicals studied, Kahlbaum's pure liquids were used as obtained, and in the case of water the vessel was overflowed with it, and after allowing it to rest for a while, the surface was renewed by suddenly blowing off the excess of liquid. Observations were made with clean water and also when it was contaminated with monomolecular films of oleic and palmitic acids. The following Table contains a list of the liquids, their formulæ, refractive indices, and their ellipticity coefficients as determined.

Discussion of Results.

It will be seen from the table that all the clean liquid surfaces studied showed a positive ellipticity irrespective of the value of the refractive index, and in fact there does not

Substance.	Formula.	μ_F.	K.	$t\times10^8$ cm.	Molecular diameter $\times10^8$.
Methyl alcohol ...	CH_3OH	1·329	·00069	4·7	4·0
Ethyl „ ...	C_2H_5OH	1·363	·00066	4·0	5·2
n-Propyl „ ...	C_3H_7OH	1·385	·00090	5·0	
i-Propyl „ ...	C_3H_7OH	1·380	·00100	6·4	
n-Butyl „ ...	C_4H_9OH	1·400	·00092	5·1	
i-Butyl „ ...	C_4H_9OH	1·397	·00087	5·0	
Allyl „ ...	C_3H_5OH	1·419	·00110	6·0	
Amylene	C_5H_{10}	1·381	·00150	8·8	
Pentane	C_5H_{12}	1·353	·00170	10·7	
Octane	C_8H_{18}	1·396	·00066	4·0	
Water	H_2O	1·336	·00075 ·00042 (R)*	5·0 3·0	2·6
Acetone	C_3H_6O	1·369	·00081	5·0	7·1
Carbon disulphide .	CS_2	1·642	·00142	4·6	7·3
Benzene	C_6H_6	1·507	·00107	4·8	4·1
Toluene	$C_6H_5.CH_3$	1·501	·00194	8·5	
m-Xylene	$C_6H_4(CH_3)_2$	1·502	·00202	9·0	
Nitro-benzene	$C_6H_5(NO_2)$	1·548	·00131	5·2	
Carbon tetrachloride	CCl_4	1·462	·00084	4·0	
Oleic acid.....	$C_{17}H_{33}.COOH$	1·460	·00210	12·6	
Oleic acid film on water.	.....	...	minus ·00240	13·3	11·2
Palmitic acid	$C_{15}H_{31}.COOH$	1·444	·00190	11·4	
Palmitic acid film on water.	.....	...	minus ·00180	10·0	24·0

* (R) refers to Rayleigh's value.

appear to be any marked correlation between the refractive index of the liquid and the magnitude of the ellipticity. This fact when considered in the light of the theoretical discussion of the effect of a transition-layer given by Drude † seems to render it unlikely that the observed ellipticity is due to any film adsorbed on the liquid surface from the atmosphere. Another explanation which might be suggested is that the molecules at the surface are orientated, and that consequently the refrangibility of the surface-layer is different from that of the inside. It is difficult, however, on this hypothesis to see why the surface-layer should always have a lower refrangibility than the interior of the liquid, which

† Drude, 'Theory of Optics,' English Translation, p. 292.

is necessary in order to explain the observed positive values of the ellipticity. An orientation of the molecules would tend rather to pack them closer together, and thus to increase the optical density of the surface-layer. Nor would any double-refraction which such an orientated film might possess help materially in explaining the observed effects. The only possibility left is that the effect arises from a diminution of the density of the surface-layer resulting from molecular movement*. Such an explanation (suggested originally by van der Waals, we believe) would seem worthy of consideration, the more especially in view of the fact that the thermal agitation of the liquid surface has been observed and the optical effects resulting from it actually measured in our studies on light-scattering. We hope later to examine very closely the question whether our results for the ellipticity are quantitatively in agreement with the extent of the thermal agitation as determined from thermodynamical principles. Meanwhile, however, we have thought it advisable to publish the observations such as they are. In the fourth column of the table are given the values for the *minimum thickness* t of the transition layer at room temperature for each liquid calculated on the assumption that the refractive index of the transition layer is the square root of the refractive index of the liquid in bulk. Drude's formula for this case is

$$t = \frac{k\lambda}{\pi} \cdot \frac{n+1}{\sqrt{1+n^2(n-1)}},$$

where λ is the wave-length and n the refractive index of the liquid. For the two contaminated surfaces of water the thickness t is calculated from Drude's general expression suitably modified,

$$t = -\frac{k\lambda}{\pi} \cdot \frac{(n_2^2-1)\,n_1^2}{\sqrt{1+n_2^2(n_1^2-1)\,(n_1^2-n_2^2)}},$$

where n_1 is the refractive index of the film assumed to be the geometric mean of the refractive index of the material in bulk and of water, and n_2 is the refractive index of water.

The thickness of the transition layer for the various pure liquid surfaces comes out to be of the same order of magnitude as the linear dimensions of the molecule (see column 6 of the table where molecular diameters from viscosity measurements etc. are given). In the case of the contaminated water-surfaces the superficial film is shown by the observations of ellipticity to be mono-molecular.

210 Bowbazaar Street, Calcutta, India.
24th June, 1926.

* L. P. Wheeler, Phil. Mag. vol. xxii. p. 229 (1911).

XXI. *Photographs of the Flow round a Model Screw working in Water, especially in the "Vortex Ring State."* By C. N. H. Lock, *M.A.*, *and* H. C. H. Townend, *B.Sc.*, *of the Aerodynamics Department, National Physical Laboratory* *.

[Plates IV.–VI.]

1. *Introduction.*

THE modern theory of the action of an airscrew is based on the assumption that any blade element, in its motion through air in a helical path, reacts with the fluid in the same way as a similar element of an aerofoil moving in a straight path. The crudest possible assumption is that the forces on the blade element depend only on its shape and absolute motion. Actually, in virtue of the "thrust" exerted by the screw, there will be a general motion of the fluid through the screw in the direction of the thrust. If the mean value of this "axial interference velocity" is known, it may be combined with the absolute velocities of the aerofoil elements to give their true velocity relative to the fluid. In order to determine the axial interference velocity, it is convenient to consider the screw as an "actuator," *i.e.*, a distribution of external forces which act on the fluid in the direction of the axis of the screw without introducing any obstacle to the flow; as a first approximation the force per unit area is assumed to be uniform over the airscrew disk. It is required to determine a velocity field which will correspond to any given relation between the thrust and the velocity of advance of the screw through still air, the most important detail being the mean velocity through the airscrew disk.

Over a certain range, which includes moderate values of the thrust, considerable progress has been made in determining the general velocity field and in particular the mean velocity through the airscrew disk, from consideration of the general dynamics of the air flow †. For extreme values of the thrust, where these methods break down, an attempt has recently been made to obtain an empirical relation to determine the velocity through the airscrew disk, by analysing some experiments (undertaken

* Communicated by Mr. E. F. Relf, A.R.C.S., by permission of the Aeronautical Research Committee.

† See especially "An Aerodynamic Theory of the Airscrew," by H. Glauert. Aeronautical Research Committee Reports and Memoranda, No. 786.

specially for this purpose) * on model airscrews in a wind tunnel. These experiments comprised measurements of thrust and torque on the airscrews for known values of the tunnel velocity and rotational speed, but did not include direct measurements of velocity near the airscrew, so that the general velocity field remained unknown. It was therefore suggested by Professor G. I. Taylor that it would be of interest to observe the actual velocity field under these extreme conditions, by photographing the flow round a screw working in water. These photographs form the subject of the present paper.

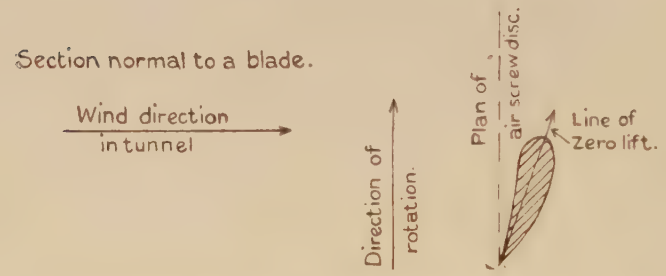
2. *Classification of the Working States of a Screw.*

In all the experiments, both in air and water, the screw rotated at a fixed point and a stream of fluid was caused to flow past it by external means. It will therefore be convenient to refer all fluid velocities to the centre of the screw. It is obvious that the pitch and rotation of the screw may be so adjusted that the total thrust on the screw is zero; it will be assumed that the screw then produces no disturbance in the fluid, so that the mean axial velocity u through the airscrew is equal to the velocity V of the fluid stream at a distance. On altering the rotational speed a thrust is produced which is considered positive when the force on the fluid is in the same direction as u (considered positive). The possible working states of a screw can therefore be classified as follows:—(1) The "normal working state" in which the thrust is of the same sign as u and therefore tends to increase u, so that u is greater than V. (2) The "Windmill brake state" in which the thrust is negative when u is positive, so that u is less than V. (3) There is also the third possibility that u and V may be of opposite sign. Suppose that the wind direction relative to the screw is as shown in fig. 1. Then the tunnel velocity V is called negative for a positive blade angle; the screw tends to drive the fluid against the general stream, and will actually do so if the ratio of rotational speed to tunnel velocity is sufficiently high. The mean axial velocity u through the airscrew disk relative

* See "An Extension of the Vortex Theory of Airscrews, with Experimental Results," by C. N. H. Lock, H. Bateman, and H. C. H. Townend. Aeronautical Research Committee Reports and Memoranda, No. 1014. Also "The Analysis of Experimental Results in the Windmill Brake and Vortex Ring States of an Airscrew," by H. Glauert. Reports and Memoranda, No. 1026.

to the screw is then opposed to the tunnel velocity, so that u and V are of opposite sign, and the screw is said to be working in the "vortex ring state." This name was suggested by the fact that the fluid flowing through the airscrew disk against the general stream must return outside it, so that the flow must bear some resemblance to a circular vortex ring.

Fig. 1.



The theoretical methods of determining the flow can be applied throughout the greater part of the normal and windmill brake states, but not in the vortex ring state. It was to this latter state, and to part of the windmill brake state, that the methods of R. & M. 1014 and the photographs of the present report were chiefly directed, but some photographs of the remainder of the working range are also included for completeness.

3. *Details of the Experiment.*

The photographs shown here were taken in the small water channel of the Aerodynamics Department of the National Physical Laboratory, which is fully described in R. & M. 31*. The working section is a rectangular trough 3 inches wide by 5 inches deep in which a steady stream of about 0·5 inch/second can be obtained. A model two-bladed airscrew of 1 inch diameter was constructed of gunmetal and driven by an electric motor, to which it was connected through a flexible shaft. A photograph of the screw is given in fig. 2 (Pl. IV.).

* Apparatus for the visual and photographic study of the Distribution of the Flow round models in a Current of Water, by C. G. Eden. R. & M. 31. Technical Report of the Advisory Committee for Aeronautics 1910–11, p. 48.—Also R. & M. 76. Technical Reports 1912–1913. Photographs of the flow round a model aerofoil, by E. F. Relf.

The screw is of constant geometrical pitch* 0·15 inch and maximum blade width 0·17 inch. In other respects the blades are roughly scale models of a blade of the family of airscrews †. The rotational speed could be varied from about 1 to 20 revolutions per second.

The flow was rendered visible by a spray of drops of oil (xylene and carbon tetrachloride) discharged into the water at a point some distance upstream from the model. The density of this oil is equal to that of water, while the refractive index is such that a ray of light is deflected through a right angle by a spherical drop. The photographs were taken from a point vertically above the model, and the illumination by a pair of arc lights was limited to a horizontal band $\frac{3}{16}$ inch deep intersecting the axis of the screw and extending right across the channel. Exposures varied from 1 second to 2 seconds so that the length of the streak representing the path of an oil drop varies from $\frac{1}{2}$ to 1 inch in the undisturbed stream.

4. *Description of the Photographs.*

In all cases the photographs are arranged with the flat under surface of the screw to the right, and the screw is rotating with its leading edges forward so that it always tends to move the fluid from left to right. In the first series of 4 photographs (figs. 3–6, Pls. IV. and V.) V is negative, *i.e.*, the general stream is from right to left. The rotational speed increases successively from the first to the fourth photograph, the velocity of the stream being kept constant. In fig. 3 there appears to be a small velocity through the screw from right to left so that u/V is positive, but u is less than V, so that we have the windmill brake state. In figs. 5 and 6, u/V is certainly negative and we have the vortex ring state, as also probably in fig. 4. In figs. 4–6 there is evidence of a distinct circular vortex ring whose core is to the left of the screw in fig. 4, but to the right in figs. 5 and 6.

Fig. 7 (Pl. V.) was taken with the screw at rest, to show the degree of steadiness of the undisturbed stream.

In figs. 8, 9 and 10 (Pl. VI.) the direction of the stream is reversed relative to the screw, being now from left to right,

* If the flat under surface of the blade at radius r makes an angle θ with the plane of rotation, the pitch at that radius is given by the relation $\text{pitch} = 2\pi r \tan\theta$.

† "Experiments with a Family of Airscrews," by A. Fage and others. A.R.C. R. & M. 829.

and we have the more usual condition of working of a screw. The rotational speed increases from fig. 8 to fig. 10. In fig. 8, the rotational speed is so slow that the fluid is retarded on passing through the screw (u is less than V), and we have the windmill brake state as in fig. 3. In fig. 9, u is approximately equal to V and we have the condition of zero thrust. In fig. 10, u is greater than V and we have the normal working state of a screw developing a positive thrust.

5. *Discussion of the Results.*

The photographs of the "vortex ring state" (figs. 4–6) show a considerable turbulence around the screw, but the actual degree of turbulence can best be judged by visual observation. For example, it might be supposed from the appearance of the vortex ring in fig. 5 that most of the fluid which actually passes through the screw circulates continually in a closed path. But visual observations indicate that this is not the case; on watching individual oil drops it appears that few of them pass through the screw a second time and very few a third time, their motion being wildly irregular and involving a thorough mixing up outside the screw. In fact, the real flow is even more turbulent than the photographs suggest. It is also obvious that the constraint of the boundaries of the stream exerts a considerable influence on the velocity distribution, although the constriction is considerably less than that for a 3-foot screw working in a 7-foot tunnel as in the experiments of R. & M. 1014. It must be remembered, however, that in the limiting case of V zero the water channel has virtually closed ends as opposed to the open ends of the wind channel.

Somewhat contrary to expectation fig. 10 shows considerable turbulence behind the screw in the normal working state. It seems that the screw has a considerable centrifugal effect, and so tends to break up the stream as it passes through it. It is possible that this effect is due to the very small scale of the experiments.

XXII. *The "Flash" Arc Spectrum of Rubidium.* By F. H. Newman, *D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter* *.

[Plate VII.]

1. Introduction.

Goldstein † found that by passing a high current density electrical discharge through salts of the alkali metals he could obtain new series spectra of these metals. He gave the name "ground spectra" to these spectra. Nelthorpe ‡, using a method similar to that employed by Goldstein, found that if an intense electrical discharge was sent at very low vapour pressure through rubidium fluoride, packed round the electrodes, only rubidium spark lines appeared in the resulting spectra. Exner and Haschek § investigated the spark spectrum of rubidium, and they measured the wave-lengths of the spark lines, which in many cases corresponded to the enhanced lines indicated by Lockyer ‖. Another type of rubidium spectrum has been found by Dunoyer ¶, who used an experimental method different from that employed by other investigators. It has long been known that a gas at low pressure becomes luminous when the tube in which it is contained is placed in an alternating electromagnetic field of high frequency. Dunoyer investigated the excitation conditions for the luminescence, and the spectra of the radiation produced, when rubidium and cæsium vapours were present in the tube. He found that brilliant radiation was obtained with these vapours at temperatures between 100° and 300° C. Certain changes in the colour of the radiation were noted, these changes depending on the temperature and on the degree of electrical stimulus employed. Nearly all of the rubidium spark and enhanced lines measured by Exner and Haschek and Lockyer were found among the most intense of the lines occurring in Dunoyer's induction spectra. Some of the spark lines, such as λ 3353·5, 3861·4, 3914·15, 4132·70, 4188·15, were very feeble in the induction spectra, and the latter contained several bright lines not previously noted as

* Communicated by the Author.
† Astrophys. Journ. xxvii. p. 25 (1908).
‡ Astrophys. Journ. xli. p. 16 (1915).
§ *Die Spectren der Elemente bei normalem Druck* (1911).
‖ See Kayser's *Handbuch der Spectroscopie* (1912).
¶ *J. de Phys. et le Rad.* iii. p. 261 (1922).

spark and enhanced lines such as λ 3433·8, 3461·4, 3662·6, 4348 3. Many of the lines indicated by Goldstein as belonging to the "ground spectra" were present among Dunoyer's results, but, with the exception of the doublet λ 4201, 4215, no flame or arc lines were noted. This absence of the principal and subordinate series lines in the induction spectra indicates the predominance of ionized vapour atoms during excitation of the vapour.

The doublet system of the alkali metals is the typical arc spectrum, being derived from the neutral atom, but the disruption of the valency electron displaces the atom of the alkali into the column of inert gases, so that spectroscopically this signifies the transition from the simple doublet system to a many-lined spectrum resembling the complicated spectra of the inert gases. For example, when the outer electron is removed from rubidium atoms the configuration of the electrons remaining is identical with the extra-nuclear electron system responsible for the ordinary arc spectrum of krypton. The only difference between the rubidium spark and the krypton arc spectra one would expect is that, as the nuclear charge is one unit higher in rubidium than in krypton, the spark spectrum of rubidium should appear farther down in the ultra-violet region than that of the krypton arc.

Krypton exhibits at least two types of spectra. Merrill * found that its spectrum possessed a group of very strong lines in the red with the further characteristic that the shortest lines of the group were especially strong, and that in the direction of the violet from these lines lay a region containing only weak lines. Bloch and Dejardin † found that the first spark spectrum of krypton extended from the extreme red to the extreme violet. The second spark spectrum, much less rich in lines, commenced sharply at the border of the violet and the ultra-violet regions. The third spark spectrum has many more lines in the ultra-violet than in the visible region, so it is evident that at least two spectra may be obtained. The first containing many lines in the visible is excited with the ordinary electrical discharge, while the second group of lines lying in the ultra-violet is stimulated by a condensed discharge. In a similar manner, by varying the degree of electrical excitation, it should be possible to obtain in the case of ionized rubidium

* Bureau of Standards Bull. 15, p. 251. Scientific Papers, No. 345 (1919).

† *Comptes Rendus*, clxxviii. p. 766 (1924); and *Ann. d. Phys.* ii. p. 461 (1924).

two groups of lines analogous to the two krypton arc spectra. The author * has already succeeded in producing a group of potassium spark lines analogous to the argon red spectrum, and in the present work it is shown that a group of rubidium spark lines corresponding to the krypton red spectrum may be excited in a similar manner.

2. Experiments.

Under ordinary conditions the arc spectra of many elements contain some enhanced lines, although they are not, as a rule, very bright. If an interrupted arc is used, *i.e.* an intermittent arc, then the enhanced lines may appear in some cases more intense than the ordinary arc lines. This is particularly the case with potassium, the flash arc spectrum of this element consisting almost entirely of the so-called spark lines.

In the present experiments the three-electrode arc discharge tube was made of glass and was sealed at one end by means of a quartz window. One of the iron electrodes was enclosed in a glass tube, and into the end of this tube was packed some rubidium metal, so that an arc could be struck between this metal, which was made the cathode, and the second iron arc electrode. The third electrode enabled the arc to be started by passing a momentary electric discharge by means of an induction coil. Using a special rotating commutator, this rubidium arc could be alternately started and quenched, and the radiation from the rubidium cathode was focussed by means of a quartz lens on to the slit of a quartz spectrograph. The resulting spectra were photographed on special rapid panchromatic plates. The discharge tube was connected to a pump which, running continuously, maintained the residual gas-pressure below 10^{-3} mm. of mercury. The applied potential difference was 120 volts, and with this arrangement a steady arc through rubidium vapour could be maintained.

The radiation from the intermittent or flash arc appeared lilac in colour, and when examined by means of the spectrograph showed most of the enhanced lines of rubidium down to λ 3080 in addition to the ordinary arc lines. With potassium it had been possible to excite in a similar manner the so-called spark lines without the ordinary arc lines, but this was not possible with rubidium, although the spark lines of this metal were much brighter than the arc lines.

The various lines appearing in the flash arc spectrum were

* Phil. Mag. ii. p. 1042 (1926).

measured, and are given in Table I. The principal and subordinate series lines are not included in this table. For the sake of comparison the spark lines measured by Exner and Haschek and the induction spectra lines of Dunoyer have been included.

TABLE I.

"Flash" Arc Spectrum of Rubidium.

Flash arc.		Spark (Exner and Haschek).		Induction (Dunoyer).	
Wave-Length.	Intensity.	Wave-Length.	Intensity.	Wave-Length.	Intensity.
6517	0	—	—	—	—
6466	0	—	—	—	—
5525	1	—	—	5524·7	1
5154	2	—	—	5154·3	4
5076	0	—	—	—	—
4934	0	—	—	—	—
4886	2	—	—	4886·0	5
4784	3	—	—	4785·2	8
4776	10	4777·5	2	4776·3	40
4763	5	—	—	—	
4740	1	—	—	—	—
4686	0	—	—	—	—
4658	2	—	—	4657·9	4
4649	7	4648·75	2	4648·4	20
4623	3	4622·55	1	4622·6	10
4572	10	4571·75	8	4572·3	40
4541	3	—	—	4540·7	5
4531	4	4530·5	1	4530·5	20
4497	1	—	—	—	—
4470	4	—	—	4469·7	8
4441	0	—	—	4440·2	5
4378	9	4378·1	1	4377·9	40
4348	4	—	—	4348·3	40
4344	0	—	—	4343·6	0·5
4306	3	—	—	4306·6	4
4295	10	4294·08	10	4294·3	50
4288	3	4288·2	2	4288·2	40
4273	9	4273·26	3	4273·0	50
4267	3	—	—	4266·4	10
4243	12	4244·5	30	4242·6	50
4193	4	4193·18	3	4193·2	20
4179	0	—	—	4179·0	1
4136	4	4136·55	1	4136·4	20
4105	8	4104·49	10	4105·2	30
4085	3	4084·05	2	4084·3	20
4029	2	4029·65	1	—	—
3978	4	3978·30	2	3978·0	20
3941	10	3940·62	20	3941·1	40
3927	8	3927·3	1	3926·4	12
3915	0	3914·5	1	3914·7	1
3872	0	—	—	—	—

TABLE I. (*continued*).

Flash arc.		Spark (Exner and Haschek).		Induction (Dunoyer).	
Wave-Length.	Inteusity.	Wave-Length.	Intensity.	Wave-Length.	Intensity.
3861	1	3861·40	5	3861·2	2
3827	5	3828·1	2	3827·2	20
3802	4	3802·05	2	3802·1	30
3797	5	3796·99	3	3797·3	40
3746	1	—	—	3746·5	6
3700	4	3699·98	1	3699·8	15
3664	6	3664·4	1	3663·8	10
3663	6	3663·5	1	3662·6	20
3647	0	—	—	3646·3	8
3640	3	3640·55	1	3639·7	10
3601	7	3601·35	3	3600·4	30
3577	0	—	—	3576·8	6
3542	1	—	—	3541·4	8
3532	3	3532·2	1	3531·9	10
3522	5	3522·2	2	3521·5	15
3461·1	2	—	—	3461·4	10
3434·4	1	—	—	3433·8	12
3416·2	0	—	—	3415·6	6
3393·4	3	3393·7	1	3393·2	8
3375·4	0	—	—	3375·3	2
3354·1	1	3353·5	2	3354·3	3
3341·0	3	3341·2	1	3341·4	10
3271·4	2	3271·6	1	3271·0	10
3223·2	0	3222·7	1	3223·4	10
3149·4	0	—	—	3149·3	5
3112·1	0	—	—	3111·7	5
3093·5	0	—	—	3093·8	4
3081·6	0	—	—	—	—

A perusal of Table I. shows that practically all of the spark lines noted by Exner and Haschek appear in the flash arc spectrum, although the following lines of the spark spectrum are missing. λ 3851·9, 3833·94, 3492·50, 3321·61, 3286·6. In a similar manner all of the flash arc lines are amongst Dunoyer's induction spectra lines except one or two faint ones, but λ 4763, which is bright in the flash arc, is not given in the tables of the other experimenters. In some cases the relative brightness of the lines is different. For example, in the induction spectra λ 4377·9 and 4348·3 are of equal intensity, whereas in the flash spectrum λ 4378 has intensity 9 and λ 4348 intensity 4, but the greatly-increased stimulus used in the electromagnetic excitation must necessarily entail a redistribution of intensity among the various lines. In connexion with this, it is interesting to note that the two lines λ 4295, 4288, have the same relative intensities

in the flash arc and the spark spectra, but not in the induction spectrum.

The flash arc spectrum, containing as it does most of the enhanced lines of wave-lengths greater than λ 3080, differs considerably from the ordinary rubidium arc spectrum. This is shown in spectrograms Nos. I. and II. (Pl. VII.) From the reproductions shown in the Plate, it will be seen that the wave-lengths in the flash arc spectrum fall into a region, the optical or spectral centre of gravity of which is approximately at λ=4070. This group of enhanced lines, lying within the region λ 5525–λ 3271·4, is analogous to the krypton "red" arc spectrum, both groups of lines being excited by relatively low electrical stimulus.

It was found that if rubidium fluoride salt was substituted for the metal an arc could be passed between this salt and the iron electrode. The radiation, photographed by means of the spectrograph, showed many enhanced lines of rubidium in addition to the ordinary arc lines (Spectrogram No. III., Pl. VII.). The spectrum is intermediate in nature between the rubidium arc spectrum and that obtained with the flash arc. This method of investigating arc spectra with salts gives much better results than the one more usually employed, where the salt is introduced in a hole made in one of the carbons constituting the carbon arc.

Mohler * has determined the potential for the excitation of rubidium spark lines to be 16 volts, and this measures the work required to remove a single electron from the outermost complete shell, *i. e.* one N electron. The complete spark spectrum requires for its excitation the removal of one N electron, corresponding to 16 volts, followed by a 10-volt collision, through which the outer electron is removed. The total work required to remove the valency electron and one N electron is thus equal to 26 volts approximately. The energy, 10 volts, necessary to remove the second electron from its quantized orbit in the simply ionized rubidium atom can be computed from the Ritz equation. The complete spark spectrum, however, may be produced by first removing the valence electron with energy 4·2 volts, followed by the removal of the N electron at 21·8 volts and, as Mohler states, the potential 21·6 volts, which has been determined experimentally for rubidium, apparently measures the work required to remove the second electron from an ion with the valence electron already removed. From these results we may conclude that the enhanced spectrum of rubidium should accompany its N radiation at about 16 volts. It is

* Bureau of Standards Sci. Papers, No. 505, p. 167 (1925).

to be expected, therefore, that enhanced lines should appear in the rubidium arc, provided that the vapour-pressure is low. Under ordinary arc conditions the fall of potential per mean free path of the electrons is not likely to approach 16 volts, but at low pressures and with an intermittent arc, especially in the neighbourhood of the cathode where the potential gradient is high, the voltage per mean free path of an appreciable fraction of the number of electrons present may exceed 16 volts. If so, the spark lines are developed. This is so in the present case, where the actual potential differences between the electrodes at each flash, or at any rate for a considerable period of each flash, will be the full applied potential difference, viz. 120 volts.

As stated above, the optical centre of the group of enhanced lines developed in the flash arc is at λ 4070 approximately, the excitation voltage being too small to excite the lines in the far ultra-violet. The development in this manner of a spark spectrum analogous in structure to the many-lined krypton arc "red" spectrum emphasizes the similarity in structure of the ionized rubidium and the normal krypton atoms.

The author wishes to express his thanks to the Royal Society for a Government Grant, which enabled this research to be carried out.

XXIII. *On the Potential Difference across a Semi-Permeable Membrane.* *By* Dr. Naota Kameyama *.

IF there be an unequal distribution of K^+-ions between two electrolyte solutions separated by a semi-permeable membrane (due to the presence of certain ions which cannot pass through the membrane), there will be set up a potential difference across the membrane. The value of this potential difference is given by the following formula from the thermodynamical theory of the membrane equilibrium †:

$$E_m = \frac{RT}{F} Ln \frac{[K]_1}{[K]_2} = \frac{RT}{F} Ln \frac{m_1 f_1}{m_2 f_2}, \quad . \quad . \quad . \quad (1)$$

where $[K]$, f, and m (with suffix) represent the activity, activity coefficient, and molarity of K^+-ion in each solution. The sign of E_m is such that, if m_1 is greater than m_2, the positive current tends to flow from compartment 1 to compartment 2 through the membrane. Such a case is given by

* Communicated by Prof. F. G. Donnan, F.R.S.

† F. G. Donnan, *Z. f. Elektroch.* xvii. p. 572 (1911).

the system composed of a solution of potassium chloride and a mixed solution of chloride and ferrocyanide of potassium; or the system composed of two solutions of potassium ferrocyanide of different concentrations, both separated by copper ferrocyanide membranes: or the system of Congo-red as non-diffusing electrolyte and sodium chloride as the distributing salt.

The object of the present investigation is the experimental test of the above relation in the case of potassium ferrocyanide solutions of different concentrations. At the outset it was not found feasible (though very desirable) to determine independently the activity of potassium ions in the ferrocyanide solutions and apply the values in the above formula, in order to see whether the equation holds or not. Therefore the following scheme has been taken instead. A chain:

Potassium amalgam | K_4FeCy_6 ‖ K_4FeCy_6 | Potassium amalgam, has been made,‖ being the copper ferrocyanide membrane, and the e.m.f. measured. Here two electrodes made of the same sample of amalgam were used at both ends of the chain. As the amalgam electrode is reversible with respect to K^+-ions, a concentration cell of K^+-ions is set up at the ends of the chain, the e.m.f. of which is given by the following formula:

$$E_c = -\frac{RT}{F} Ln \frac{[K]_1}{[K]_2} = -\frac{RT}{F} Ln \frac{m_1 f_1}{m_2 f_2}, \quad . \quad . \quad (2)$$

that is, E_c is equal to E_m in magnitude and of opposite sign. Consequently E, the total e.m.f. of the chain, being the sum of the two, should be zero. As the nature of the concentration cell is well known, the nullity of e.m.f. of the chain may be taken as a proof of the existence of the relation represented by equation 1.

Experimental.

The potassium amalgams used were prepared in the way prescribed by G. N. Lewis and F. G. Keyes *, with mercury purified by pouring through a column of nitric acid several times and by distillation *in vacuo*. The concentrations of potassium in the amalgam were 0·262 per cent. in the case of the A-series and 0·129 per cent. in the case of the B-series. A pair of electrodes made from the same sample of amalgam were used in each experiment. The equality of the pair of electrodes with respect to e.m.f. was examined by dipping both of them in a solution of potassium chloride, and then measuring the potential difference across them. In both

* J. Amer. Chem. Soc. xxxiv. p. 119 (1912).

series of experiments, A and B, the differences of electrode potential were never more than 0·03 millivolt, an amount of little importance in the present work.

The membranes were prepared in the usual way. A piece of vegetable parchment spread over a shallow wide glass cylinder was placed in a porcelain basin, 0·2 M. copper sulphate solution being put on one side of the membrane, and 0·1 M. potassium ferrocyanide solution on the other *. The solutions were interchanged every day for about five days, after which the membrane was thoroughly washed and tested for semi-permeability. The test was done in the membrane-vessel with 0·05 M. ferrocyanide on one side and the nearly isotonic sucrose solution, 50·52 grams per litre, in the other. No detectable amount of ferrocyanide was found passing through the membrane after several days. In order to test the equality of the two sides of the membrane with respect to potential difference, both the compartments of the membrane-vessel were filled with one and the same solution of ferrocyanide (0·0049 M.), and the e.m.f. across the membrane was measured with the amalgam electrodes at both ends. The result was 0·06 millivolt, of which about 0·03 millivolt was covered by the difference of the electrodes.

The membrane-vessel consisted of a pair of shallow wide glass cylinders with flat flanges, pressed tightly together by means of a clamp and holding the membrane between them. Each of the two compartments so formed was connected by means of a wide tube to a glass cylinder in which the amalgam electrode was inserted. The part of the system on one side of the membrane, comprising the membrane-vessel compartment, the connecting-tube, and the electrode-carrying cylinder, was filled with a ferrocyanide solution, and the other side with another ferrocyanide solution of different concentration. The stronger solution was kept 0·05 M., except in the case of the last experiment, and the weaker one was changed from 0·05 M. to 0·0005 M. in steps. To make the dilute solution, for instance 0·005 M. solution, 100 c.c. of 0·05 M. solution (without sucrose) was taken in a litre flask and made up to a litre with a sucrose solution (50·52 grams per litre), which is nearly isotonic with the 0·05 M. solution. In the last experiment no sucrose was used. The presence of sucrose causes an effect upon the activity coefficients of the ions, though equations 1 and 2 still hold good.

The e.m.f. measurements were made with frequent renewal of the amalgam surface, sometimes with continuous dropping of amalgam. The solution in the electrode

* The symbol M denotes gram mols per litre.

chamber was also renewed frequently, being sometimes allowed to flow continuously during the experiment. The results with the fresh surface agreed among themselves except in very dilute solutions. Owing to the fairly large electrical resistance of the circuit and to the smallness of the e.m.f. to be measured, the following device was used for the measurement. For instance, exactly m millivolts are shunted from the potentiometric circuit to the circuit which comprises the chain to be measured, a galvanometer and a switch. The galvanometer deflexion is read. Let the reading be a mm., this corresponds to $(m+x)$ millivolts, where x represents the e.m.f. of the chain. Next, by means of the switch, the connexion of the chain is reversed, other things being kept unchanged, and again the galvanometer reading is taken. Let this be b mm., corresponding to $(m-x)$ millivolts. From a, b, and m we can easily calculate x. In both measurements the total resistance of the circuit does not change.

It was found that constancy of the e.m.f. is rapidly attained and preserved over an extended period of time. In the A-series of experiments, measurements were made on the day of setting up the solution as well as on the following days, for example, up to the 7th, 4th, 12th, and 3rd days in Exps. 1, 2, 3 and 4 respectively. The values obtained were, however, practically equal to those obtained on the first day. In the B-series, the measurements were carried out only on the first day.

Experimental Results and Discussion.

The results are given in the following table. They refer to room-temperature (*ca.* 20° C). The positive sign of the e.m.f. has been given when the positive current tends to flow from compartment 1 to 2 through the membrane in the system. Concentrations are given in millimols per litre.

The amount of the total e.m.f. did not exceed a millivolt unless a solution weaker than 0·005 M. was involved. It is remarkable that, in all the experiments except the last one, the electrode in the weaker solution was positive. This means that potassium ion tends to discharge at the electrode in the weaker solution and potassium to get ionized at the other electrode. This may possibly be explained by assuming the decomposition of the amalgam in the weaker solution, which would cause a local rise of concentration of potassium ions around the electrode, and make the electrode more positive than it should have been. The effect must be more marked in the dilute solution. This may account for the sign of the e.m.f. as well as for the fact that the

Experimental Data.					Calculated Values.		
Exp.	Concentration of Solution.			E.	Activity Coefficient.		E_m.
No.	m_1.	m_2.	m_1/m_2.	Millivolts.	f_1.	f_2.	Millivolts.
Series A.							
1	50	25	2	0·2–0·4	0·682	0·733	16
2	50	10	5	0·6–0·7	0·682	0·794	37
3	50	5	10	0·6–0·7	0·682	0·840	53
4	50	0·5	100	16–17	0·682	0·946	108
Series B.							
5	50	5	10	0·5–0·6	0·682	0·840	53
6	50	1·5	33	3·6–4·0	0·682	0·905	81
7	50	0·5	100	7	0·682	0·946	108
8	490	4·9	100	−1·6	—	0·841	—

deviation increased as the dilution increased. Perhaps such a dilute solution as 0·0005 M. may have been beyond the limit of availability for the particular concentrations of the amalgam here used. In the last experiment a very concentrated solution was used on one side for the purpose of getting the greatest difference of concentration and still avoiding the use of too dilute a solution. In this case the e.m.f. was much smaller than in the case of Exp. 4 or of Exp. 7, and the sign was negative. It is quite probable that this abnormal sign was due to the slight osmosis of water from compartment 2 to 1 through the membrane, thereby decreasing the concentration difference at the membrane, as no sucrose was added in this experiment to counteract the osmotic pressure in compartment 1.

Although it seems impossible at present to determine the values of E_m or E_c exactly, even approximate values may help us to get an idea of the extent to which the experiments agreed with the theoretical requirement. For this purpose a calculation of the activity coefficients of potassium ions has been made, and E_m calculated therefrom, these values being given in the sixth and seventh columns of the table. The assumption that has been made for the calculation is the "ionic strength principle" of G. N. Lewis as applied to individual ions *. It is generally agreed that f_K is nearly

* G. N. Lewis and M. Randall, 'Thermodynamics,' p. 380.

equal to f_{Cl} in the same solution *, therefore f_K may be taken as equal to f_{KCl}, the "mean" activity coefficient of KCl in the same solution, which is defined as $\sqrt{f_K \cdot f_{Cl}}$. Now, in another experiment of the author †, it has been found that f_{KCl} is almost unchanged when the greater part of the KCl is replaced by $K_4(FeCy)_6$ of equal "ionic strength," μ. Therefore we may not be in great error if we assume that f_K in a $K_4(FeCy)_6$ solution is equal to the f_{KCl} of KCl in a pure KCl solution which has the same μ as the ferrocyanide solution. Hence the f's were interpolated at the requisite values of μ on the curve of f_{KCl} against $\mu^{\frac{1}{2}}$ for a pure KCl solution at 25°. The effect of temperature on f_1/f_2 is not appreciable in the present case. T in Equation 1 was put equal to 293°.

Perhaps the presence of sugar ‡ increases the activity of the potassium ion, but the effect was not taken into account, as the concentration of sugar, varying according to the concentration of the ferrocyanide, did not reach 5 per cent.

With such reserve, we see that E_m is equal to E_c within 2 per cent., except when a very dilute solution is involved.

Summary.

It has been tested experimentally whether the potential difference across a copper ferrocyanide membrane in the system $K_4(FeCy)_6(m_1) \parallel K_4(FeCy)_6(m_2)$ is given by

$$E_m = \frac{RT}{F} Ln \frac{[K]_1}{[K]_2},$$

where [K] represent the activity of potassium ion. For this purpose the following chain was set up K-amalgam | $K_4FeCy_6(m_1) \parallel K_4FeCy_6(m_2)$ K-amalgam. Here E_m is just balanced by the concentration cell with respect to K^+-ion at the ends of the chain. The nullity of the total e.m.f. is taken as a verification of the above relation. The results confirm the theory in so far as the solutions involved are not so dilute as to produce disturbing effects caused by interaction of the amalgam with water.

In conclusion the author desires to express his sincere thanks for advice to Professor F. G. Donnan, at whose suggestion the investigation was undertaken.

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* MacInnes, J. Amer. Chem. Soc. xli. p. 1086 (1919); G. N. Lewis, 'Thermodynamics,' p. 381.

† Phil. Mag. p. 851 (1925).

‡ See Corran and MacLewis, J. Amer. Chem. Soc. lxiv. p. 1673 (1922), for an effect of sucrose on Cl'-activity.

XXIV. *The Rate of Monomolecular Reactions.*

By Sir J. J. Thomson, *O.M., F.R.S.**

Summary.

Hirst and Rideal (Proc. Roy. Soc. A, cix. p. 526) have established the very interesting and important result that the rate of the monomolecular reaction $2N_2O_5 = 2N_2O_4 + O_2$ is independent of the pressure when that is greater than about ·27 mm. Hg. At pressures below this the rate increases as the pressure diminishes; the limiting value when the pressure approaches zero is about five times that at high pressures. The fact that the rate is so high at vanishingly small pressures shows that the decomposition of N_2O_5 cannot be due solely to collisions with other molecules; there must be some other agent at work, and radiation naturally suggests itself. In the paper an expression is worked out for the rate of the reaction when both collisions and radiation are taken into account. According to it the variation with pressure is of the same type as that observed by Hirst and Rideal, *i. e.* is independent of pressure above a certain pressure, but changes at low pressures. This is satisfactory as far as it goes, but the rates indicated by this expression are of quite a different order from those measured by Hirst and Rideal unless the absorption of the active radiation is on quite a different scale from that indicated by direct experiment. If the effect is due to radiation the absorption of the active rays by N_2O_5 must be so great that a layer of the gas at atmospheric pressure less than 10^{-10} cm. thick would be quite opaque to the radiation. This is quite contrary to experience, and so another way in which the decomposition may be effected is discussed in the paper. It is suggested that even in the absence of collisions and radiation the energy content of a molecule does not remain constant. It is shown that if the forces inside the molecule are intermittent instead of being perfectly continuous, then, even if the energy contents of a large number of molecules are all the same to begin with, they will not remain so, but rapidly reach a state in which the energy is distributed among the molecules in the way indicated by Maxwell's law of distribution; *i. e.*, that the chance of a molecule having energy greater than w is proportional to $\epsilon^{-\frac{w}{2w_0}}$, where w_0 is the mean energy. Thus with forces of this nature the energy

* Communicated by the Author.

content of a molecule waxes and wanes even when there is no communication of energy by collision or radiation.

The principle of the Conservation of Energy does not hold for a single molecule, though it holds on the average for a large number. An individual molecule can give energy up to or receive energy from the medium around it. As the distribution of energy in this case, as in collisions and radiation, is represented by Maxwell's law, the theory is similar to the usual one: the numerical values will, however, be different. For the rate of the reaction is not fixed by the number of molecules which at any time possess enough energy to be active; it is measured by the number which receive this energy in unit time. If N be the number of molecules having, when things are in a steady state, a particular amount of energy, the number which pass out of that state in time δt is $N\delta t/T$, where T is a certain time-constant. When things are in a steady state, the number of molecules which lose this energy in the time δt will be equal to the number which acquire it, so that N/T will measure the rate of the reaction. When the energy is conveyed to the molecules by collisions, T is equal to the average interval between the two collisions; when the energy is conveyed by radiation, T is the average interval between the collisions of a molecule with light quanta; when, however, the surging of the energy is due to the intermittence of the force, which we may regard as due to a series of impacts, T would depend on the average interval between two impacts, and may well be small compared with the interval between collisions occurring either between molecules or between molecules and light-quanta. The smaller value of T would make the rate due to this cause much more rapid than that due to radiation, or to collisions at low pressures.

We begin by finding an expression for the rate of a monomolecular reaction, *e. g.* the dissociation of a molecule into atoms, on the assumption that the dissociation is due to two causes:—

(1) The absorption of energy by collisions with very rapidly moving molecules; (2) the absorption of energy due to radiation or to some source other than the energy in the surrounding molecules.

Let w be the energy which must be communicated to a molecule of the reacting substance. Then the chance that a molecule of this substance receives in the time δt by collision with other molecules enough energy to dissociate

it can be expressed in the form

$$NA\epsilon^{-\frac{w}{R\theta}}.\,\delta t,$$

where R is the gas constant, θ the absolute temperature, N the number of molecules per unit volume, and A a function independent of N which we shall discuss later.

Let us now consider the chance of the molecules receiving the energy by the second method. This will not depend on N, and may be expressed as

$$B\epsilon^{-\frac{w}{R\theta}}.\,\delta t,$$

where B will be considered later.

We must next consider how these energized molecules may lose their energy without undergoing dissociation. As these molecules possess an exceptional amount of energy, they will lose and not gain energy by collision, so that if they make a collision before dissociation has occurred they will pass out of the class of energized molecules available for dissociation. The chance that an energized molecule should make a collision in time δt is, since its velocity is large, approximately

$$\frac{\delta t\, v_1}{\lambda},$$

where v_1 is the velocity of the energized molecule and λ the mean free path; as λ varies inversely as N, this may be written in the form $aN\,.\,\delta t$.

There may be a finite interval between the reception of the energy and the disruption of the molecule, for the energy given to the molecule may not at first be distributed in the way necessary for dissociation. To take a particular case, suppose that a complex molecule represented by A_2B_2 is struck by another molecule and receives an amount of energy w which is greater than the difference between the energy of the system A_2B_2 and that of the separate systems AB and AB. There is enough energy to dissociate the molecule provided it is properly distributed. It does not follow, however, that the communication of this energy to the molecule would at once lead to dissociation. For example, the collision might be with one of the A atoms in the molecule A_2B_2, so that, to begin with, the energy in the molecule A_2B_2 would at first be located in this A atom; if the difference between the energy of the system A_2B_2 and that of the systems A, AB_2 were greater than w, the energy given by the collision, A would not be detached and the

dissociation would not be immediate. The system for a time will remain intact; in consequence, however, of the action of the atoms in the molecule A_2B_2 on each other, the energy communicated to A will get distributed among the other atoms, and the motion of the atoms in the molecule will pass through a variety of phases. If one of these phases could be represented by two atoms, say AB, moving with the same velocity, the two remaining atoms AB having also a common velocity differing, however, from that of the first group, then since by hypothesis the difference between the energies in the systems A_2B_2 and AB + AB is less than w, the energy given to the molecule by the collision, the system when it reached this phase might dissociate.

It would, however, take time for the system to pass into this phase from that into which it was thrown by the collision. During this time it might make many collisions with other molecules, and by these collisions lose some of its energy; thus when it arrives at the phase represented by two atoms AB moving with a common velocity and two other atoms AB also moving together but with a different velocity, it may have lost so much of the energy acquired in the first collision that the energy which remains is no longer greater than the difference between that in the systems A_2B_2 and AB + AB, so that the molecule will not dissociate. Thus the effect of collisions may be two-fold: they may on the one hand give the energy required for dissociation, but on the other hand they may take it away again before it has had time to be effective.

The average time between the receipt of the energy and the dissociation may be finite. Let it be denoted by T, then the chance of an energized molecule dissociating in time δt is equal to $\delta t/\mathrm{T}$.

We are now in a position to write down equations to determine the number of energized molecules and the rate of dissociation. Let n be the number of energized molecules per unit volume, M the number of molecules per unit volume of the substance which is to dissociate, and N the whole number of molecules per unit volume; then if δn is the increase in n in the time δt, we have from the preceding investigation

$$\delta n = \delta t \left\{ \mathrm{NMA}\epsilon^{-\frac{w}{\mathrm{R}\theta}} + \mathrm{BM}\,.\,\epsilon^{-\frac{w}{\mathrm{R}\theta}} \right\} - \delta t \left(na\mathrm{N} + \frac{n}{\mathrm{T}} \right);$$

so that

$$\frac{dn}{dt} = \epsilon^{-\frac{w}{\mathrm{R}\theta}} \left\{ \mathrm{ANM} + \mathrm{BM} \right\} - n\left(a\mathrm{N} + \frac{1}{\mathrm{T}} \right) \Big\}; \quad . \quad (1)$$

and if p is the number of molecules of the product of dissociation,

$$\frac{dp}{dt} = \frac{n}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The solution of (1) is

$$n = M\epsilon^{-\frac{w}{R\theta}\frac{(AN+B)}{aN+\frac{1}{T}}} + C\epsilon^{-\left(aN+\frac{1}{T}\right)t}. \quad . \quad . \quad (3)$$

When, as in practice, t is exceedingly large compared with T, the second term on the right-hand side of (3) may be neglected, and we have

$$n = M\epsilon^{-\frac{w}{R\theta}\frac{(AN+B)}{aN+\frac{1}{T}}}$$

and

$$\frac{dp}{dt} = M\epsilon^{-\frac{w}{R\theta}}.\frac{AN+B}{aNT+1}.$$

Thus the velocity of the reaction is

$$\frac{AN+B}{aNT+1}\epsilon^{-\frac{w}{R\theta}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Let us consider how this expression varies with the pressure, which is proportional to N. We see that as long as the pressure is great enough to make AN large compared with B, and aNT large compared with 1, the velocity of reaction is $\epsilon^{-\frac{w}{R\theta}}(A/aT)$, and is independent of the pressure. When the pressure is so low that the terms in N are small compared with the others, the velocity of reaction is $B\epsilon^{-\frac{w}{R\theta}}$, and is again independent of the pressure, though its value is not the same as at high pressures. The experiments of Hirst and Rideal (*l. c.*) on the rate of decomposition of N_2O_5 show that the rate of the reaction at pressures above ·25 mm. of Hg is independent of the pressure, while at much lower pressures it increases as the pressure is diminished and approaches as the pressure approaches zero, a value about five times that at high pressures. This variation with the pressure is of the same type as that indicated by the theory. The experiments show, too, that there must be some source of dissociation other than collisions, for if there is no such source B=0, and we see from equation (4) that at low pressures the rate of reaction would diminish to zero as the

pressure falls, instead of increasing to a considerable multiple of its former value as it does according to these experiments. To compare the equation (4) with the experiments we must form an estimate of the quantities A and B, which we now proceed to do.

Let us first consider how many molecules there are which have energy greater than w, so that if their energy were transferred at a collision the molecule struck could dissociate; we do not confine ourselves to the case where the molecules are all of one kind, but include that of a dissociable molecule in an atmosphere of a neutral gas. The question arises: What kind of energy can be transformed at a collision? It seems clear that the energy due to the motion of the centre of gravity of the molecule could be so transformed. But when the molecule is one which like N_2O_5 contains a large number of atoms, the energy due to the motion of the centre of gravity may be only a comparatively small part of the total energy of the molecule; the greater part of the energy may be due to motion of the atoms relative to their centre of gravity: thus if this energy can be transferred at a collision as well as that due to the motion of the centre, there will be more molecules able to produce the "activated" state. The distribution of the internal energy among the different atoms in a complex molecule cannot be completely solved without a detailed knowledge of the structure of the molecule. We shall, however, get a superior limit to the effect produced by this internal energy if we suppose that each of the atoms in the molecule acquires and stores up energy in just the same way as if it were free, and that the collisions are effective whenever the sum of the energies of these atoms is greater than w.

Suppose that there are n atoms in the molecule. Let $v_1, v_2, \dots v_n$ denote their velocities. The chance that v_1 is between v_1 and $v_1 + dv_1$ is

$$4\frac{(hm_1)^{\frac{3}{2}}}{\sqrt{\pi}}\epsilon^{-hm_1v_1^2}v_1^2\,dv_1,$$

where m_1 is the mass of the first particle.

Hence the chance that v_1 is between v_1 and $v_1 + dv_1$, v_2 between v_2 and $v_2 + dv_2$, and so on, is

$$4\frac{(hm_1)^{\frac{3}{2}}}{\sqrt{\pi}}4\frac{(hm_2)^{\frac{3}{2}}}{\sqrt{\pi}}\dots\epsilon^{-h(m_1v_1^2+m_2v_2^2+\dots)}v_1^2\,v_2^2\dots dv_1\,dv_2\dots dv_n.$$

Let $hm_1v_1^2=\xi$, $hm_2v_2^2=\eta$, $hm_3v_3^2=\zeta$, and so on.

Thus
$$v_1^2dv=\frac{\xi^{\frac{1}{2}}}{2(hm_1)^{\frac{3}{2}}}d\xi;$$

and the chance that ξ is between ξ and $\xi + d\xi$, η between η and $\eta + d\eta$ is

$$\left(\frac{2}{\sqrt{\pi}}\right)^n \epsilon^{-(\xi+\eta+\zeta+\ldots)} \xi^{\frac{1}{2}} \eta^{\frac{1}{2}} \zeta^{\frac{1}{2}} \ldots d\xi\, d\eta\, d\zeta.$$

This is a Dirichlet integral, and the chance that $\xi+\eta+\zeta+\ldots$ is between σ and $\sigma+d\sigma$ is (Todhunter's 'Integral Calculus,' p. 262)

$$\left(\frac{2}{\sqrt{\pi}}\right)^n \frac{(\Gamma(\frac{3}{2}))^n}{\Gamma(n\times\frac{3}{2})} \epsilon^{-\sigma} \sigma^{\frac{3}{2}n-1}.d\sigma\,;$$

and the chance that σ is greater than ω is got by integrating this expression from $\sigma=\omega$ to $\sigma=\infty$.

Now,
$$\int_\omega^\infty \epsilon^{-\sigma}.\sigma^{\frac{(3n-2)}{2}} d\sigma = \epsilon^{-\omega}\omega^{\frac{3n-2}{2}}$$

approximately when, as in this case, ω is a large quantity.

Hence the chance that

$$\tfrac{1}{2}m_1v_1^2 + \tfrac{1}{2}m_2v_2^2 + \ldots$$

is greater than w is, since $\Gamma(3/2)=\sqrt{\pi}/2$,

$$\frac{1}{\Gamma(3n/2)} \cdot \left(\frac{w}{2h}\right)^{\frac{3n-2}{2}} \epsilon^{-\frac{w}{2h}}.$$

Denoting this expression for the moment by p, Np is the superior limit to the number of molecules which are able to ionize by collision. If $\bar{c}$ is the mean velocity of a molecule of the reacting substance relative to that of one of these energized molecules, and λ the mean distance the reacting molecule travels between two collisions with energized molecules, the number of activating collisions in time δt is equal to

$$\frac{\bar{c}}{\lambda}\delta t. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If Ω is the "collision area" for a molecule of the reacting substance and an energized molecule,

$$\mathrm{N}p\,\Omega\,\lambda = 1,$$

so that (5) becomes

$$\bar{c}\,\mathrm{N}p\,\Omega\,\delta t.$$

Hence with the notation of page 243,

$$\mathrm{A} = \bar{c}\,\Omega\,p\epsilon^{\frac{\omega}{2h}};$$

i. e.,
$$\mathrm{A} = \frac{\bar{c}\Omega}{\Gamma(3n/2)} \left(\frac{w}{2h}\right)^{\frac{3n-2}{2}}. \quad . \quad . \quad . \quad . \quad (6)$$

It must be remembered that this is a superior limit and not an exact estimate.

Hirst and Rideal's experiments on the dissociation of N_2O_5 enable us to test whether or not this expression gives results of the right order.

It follows from equation (4) that when the pressure is high enough to make the rate independent of the pressure, AN must be considerable compared with B. The value of B can be calculated from the rate at very low pressures which is equal to $B\epsilon^{-\frac{w}{R\theta}}$, and has been shown by Hirst and Rideal to be equal to

$$2{\cdot}53\times10^{14}\,\epsilon^{-\frac{w_0}{R\theta}},$$

where w_0 is independent of θ. To calculate the value of $NAE^{-\frac{w}{R\theta}}$, we must remember that w is the energy which has to be communicated to the molecule to activate it. The molecule struck will have some energy due to the motion of its atoms relatively to the centre of gravity; this energy will be proportional to the absolute temperature. Let it equal $qR\theta$, then if w_0 is the energy required to dissociate the molecule,

$$w+qR\theta=w_0;$$

so that

$$e^{-\frac{w}{R\theta}}=\epsilon^{q}\epsilon^{-\frac{w_0}{R\theta}}.$$

If each of the atoms in the molecule had the energy corresponding to the number of its degrees of freedom, *i. e.* had energy $R\theta/2$ corresponding to each degree of freedom, q would have its greatest value. The n atoms have $(n-1)3$ degrees of freedom relative to their centre of gravity; hence the greatest value of q is $3(n-1)/2$, and

$$NA\epsilon^{-\frac{w}{R\theta}}=\frac{Nc\Omega}{\Gamma(3n/2)}e^{3(n-1)/2}\left(\frac{w}{R\theta}\right)^{\frac{3n-2}{2}}\epsilon^{-\frac{w_0}{R\theta}}.$$

We shall suppose that the molecule of N_2O_5 behaves as if it consisted of three systems NO_2, NO_2 and O, capable of absorbing energy independently so that $n=3$. From Hirst and Rideal's experiments the value of $w_0/R\theta$ at 0° C. is in round numbers 50, and therefore if $n=3$, $w/R\theta=47$.

If N_0 is the number of molecules per c.c. of N_2O_5 at 760 mm. and 0° C., and λ_0 the mean free path of a molecule

at this temperature and pressure,

$$N_0\lambda_0\Omega = 1;$$

so that

$$NAe^{-\frac{w}{R\theta}} = \frac{N}{N_0}\frac{\bar{c}}{\lambda_0}\frac{e^3(47)^{\frac{7}{2}}}{\Gamma(9/2)}\epsilon^{-\frac{w_0}{R\theta}}$$

Taking $\bar{c} = 10^4 . \lambda_0 = 6 \times 10^{-6}$,

$$NAe^{-\frac{w}{R\theta}} = 3{\cdot}2 \times 10^{16}\frac{N}{N_0}e^{-\frac{w_0}{R\theta}},$$

and, by Hirst and Rideal's experiments,

$$B\epsilon^{-\frac{w}{R\theta}} = 2{\cdot}52 \times 10^{14}e^{-\frac{w_0}{R\theta}},$$

the ratio of these terms is $130\ N/N_0$.

Thus until N/N_0 falls to something of the order of 1/100, *i. e.* until the pressure is of the order of 7 mm., the terms depending on the collisions will be large compared with those due to the second source of ionization, and the rate will be independent of the pressure. Hirst and Rideal found that the change came at about ·27 mm.; considering the uncertainty of some of the data, the agreement between theory and experiment is perhaps as close as we could expect. The rate of the reaction at high pressures is, by equation (4),

$$\frac{A}{aT}\cdot\epsilon^{-\frac{w}{R\theta}}.$$

This, since $a = c/N_0\lambda_0$, is approximately equal to

$$\frac{1}{T}\cdot\frac{e^3(47)^{\frac{7}{2}}}{\Gamma(9/2)}\epsilon^{-\frac{w_0}{R\theta}} = \frac{2 \times 10^6}{T}\epsilon^{-\frac{w_0}{R\theta}}.$$

Hirst and Rideal find that it is equal to

$$4{\cdot}9 \times 10^{13}\epsilon^{-\frac{w_0}{R\theta}};$$

so that $T = 4{\cdot}1 \times 10^{-8}$ approximately.

Thus we see that at the higher pressures, dissociation by collisions affords a fair explanation of Hirst and Rideal's very interesting results. Below pressures of about 1 mm. our calculation shows that the rate of reaction is much greater than can be accounted for by collisions, and moreover at these low pressures the rate would fall off as the

pressure diminished if the dissociation were due to collisions: experience shows that it increases. What is the cause of the dissociation at these low pressures? We proceed to consider whether the radiation could give effects of the magnitude of those observed by Hirst and Rideal.

By Planck's law the energy streaming through unit area due to radiation whose quantum is greater than Q is

$$\int_{\nu_0}^{\infty} 8\pi . c^{-2} . \frac{h\nu^3}{\epsilon^{\frac{h\nu}{R\theta}} - 1} d\nu,$$

where c is the velocity of light and $h\nu_0 = Q$. When, as in this case, $h\nu_0$ is large compared with $R\theta$, this expression is approximately

$$8\pi c^{-2} h \int_{\nu_0}^{\infty} \nu^3 \epsilon^{-\frac{h\nu}{R\theta}} d\nu ;$$

$$8\pi c^{-2} R\theta \nu_0^3 \epsilon^{-\frac{h\nu_0}{R\theta}}$$

approximately when $h\nu_0/R\theta$ is large.

From Hirst and Rideal's experiment $h\nu_0/R\theta = 50$ at 0° C. Substituting their value of $h\nu_0$, we find that the preceding expression is equal to

$$3 \times 10^{10} \epsilon^{-\frac{\nu_0}{R\theta}} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hirst and Rideal's experiments show that at low pressures the velocity of the reaction is about

$$2{\cdot}5 \times 10^{14} \epsilon^{-\frac{Q}{R\theta}}.$$

The number of molecules in a cubic centimetre at atmospheric pressure and 0° C. is $2{\cdot}65 \times 10^{19}$; so that if the pressure is x atmospheres, the number of molecules dissociated per c.c. per second is

$$x . 2{\cdot}65 \times 10^{19} \times 2{\cdot}5 \times 10^{14} \epsilon^{-\frac{Q}{R\theta}}.$$

Since Q units of energy are absorbed when a molecule is dissociated, the energy absorbed per second per c.c. is

$$x \times Q \times 2{\cdot}65 \times 10^{19} \times 2{\cdot}5 \times 10^{14} \epsilon^{-\frac{Q}{R\theta}}.$$

Since $Q/R\theta$ is about 50 at 0° C., $Q = 1{\cdot}84 \times 10^{-12}$; hence the energy absorbed per second is approximately

$$x \times 1{\cdot}2 \times 10^{22} \epsilon^{-\frac{Q}{R\theta}}.$$

Comparing this expression for the energy absorbed per second in a cubic centimetre with that given by (7) for the energy streaming per second through the sides of the centimetre, we see that, except at infinitesimal pressures, the energy of the radiations would be quite insufficient to supply the energy required by the reaction. In other words, the external radiation would be practically all absorbed by a layer of N_2O_5 at atmospheric pressure less than 10^{-11} cm. thick. This means that even at very low pressures N_2O_5 must be quite opaque to some radiation whose wave-length is less than 10^{-4} cm. Of this we have no evidence from experiment.

Thus, in spite of the fact that if we regard decomposition as the result of a combination of the effects of collision and radiation, we can deduce an expression for the relation between rate of decomposition, pressure, and temperature which is of the right algebraical form; the values of the constants required to make this expression harmonize with the results of experiments are very different from those which would follow from anything we know about the absorption of the radiation.

We are thus driven to consider other methods of decomposition. One view we shall explore is that, owing to the character of the forces between the atoms in a molecule, there will, even in the absence of collisions and radiation, be variations in the energy content of the different molecules, and that this variation will follow a law similar to that of Maxwell for the distribution of velocities amongst the molecules of a gas. On this view there is a probability that the energy constant of a molecule may, without communication of energy by collisions and radiation, rise to a value great enough to produce the decomposition of the molecule.

Such a result would follow if the forces between the atoms in a molecule were intermittent and not continuous. On this view the existence of a force F acting on an atom would not imply that in the time δt the atom would receive an increment of momentum $F\delta t$, but that in this time there is a probability, $\delta t/T$, that the atom will receive an increment of momentum I, so that the probable increase of momentum is $I\delta t/T$. If we regard the force as due to a succession of impacts each communicating momentum I, then T is the average interval between the collisions.

To illustrate the difference between these two conceptions, consider the amount of momentum received by a body in a time t. On the hypothesis of the continuous force this will be quite definite, and equal to $\int F\,dt$. On the hypothesis of intermittent force it is not definite; thus, for

example, it is possible that in the time t no increase of momentum occurs (the probability of this is $\epsilon^{-\frac{t}{T}}$), or the body may receive one increment of momentum (the probability of this is $\frac{t}{T}\epsilon^{-\frac{t}{T}}$); the probability that it receives two increments is $\frac{1}{2!}\frac{t^2}{T^2}\epsilon^{-\frac{t}{T}}$; the probability of its receiving three is $\frac{1}{3!}\left(\frac{t}{T}\right)^3\epsilon^{-\frac{t}{T}}$; and of receiving n, $\frac{1}{n!}\left(\frac{t}{T}\right)^n\epsilon^{-\frac{t}{T}}$. The orbit which the body may describe will depend upon the number of increments of momentum it has received. Thus in this case if a body is projected from a given point with a given velocity, there will be an infinite number of possible orbits. The chance for some of them is very small: it can be shown that the orbit for which the probability is greatest is the one that approximates most closely to that which would be described under a continuous force equal to I/T. These different orbits will give rise to systems with different energy contents; for it is important to remember that the principle of the Conservation of Energy does not, when the force is intermittent, apply to individual systems, but only to the average of a large number of such systems. The energy of a single system may wax or wane without any direct transference of energy from or to other systems outside it. Thus, consider a body A describing an orbit round one of much greater mass at B. Suppose that A in going from aphelion to perihelion receives more than the average increment of momentum, while in going back from perihelion to aphelion it receives less than the average number of impacts: clearly A will gain more kinetic energy in falling to perihelion than it loses in going from perihelion to aphelion, so that the energy content will be increased on the round trip without transfer of energy from any external system. It is just as probable that A in going from aphelion to perihelion should receive fewer, and in going from perihelion to aphelion more, than the average number of increments: in this case the body will lose more energy in going from perihelion to aphelion than it gained on the approach, so that there will be a loss of energy on the round trip. Thus, if the losses are as probable as the gains, the principle of the Conservation of Energy will be true for the average of a large number of systems, though it will not hold for individual systems. We see from this illustration that even if all the systems in a large collection had the

same energy content to begin with, some in course of time would gain and others would lose energy: there would be a wide range of energy contents which in a steady state would be expressed by a distribution law.

We should for many reasons expect that the expression for the probability of an energy content w would contain a factor of the form ϵ^{-kw}. One reason is derived from an analogy with the Kinetic Theory of Gases. The difference between a continuous and an intermittent field of force may be compared with the difference between the effects when forces are transmitted through a continuous liquid or through a gas. In the first case, if coordinates fixing the position and velocity of a body immersed in the liquid are known at any time, the value of such coordinates at any future time will be determinate; when, however, the body is immersed in a gas, and the force on it conveyed by a series of impacts separated by finite times, the position and velocity of the body will not be determined uniquely by their initial values. If the masses of the body are of atomic dimensions, their energy will be distributed according to Maxwell's law of of distribution, and the expression for probability of an amount of energy w by the body would contain a factor ϵ^{-kw}.

Again, in a paper on the "Intermittence of Electric Force" (Proceedings Royal Society of Edinburgh, 46, p. 90), I have calculated the probability, when the force is intermittent, of the number of collisions in time t being p in excess or defect of the average value. The expressions for this probability are of the form $\frac{\epsilon^{-\frac{2}{2n}}}{\sqrt{2n\pi}}$ where $n=t/\mathrm{T}$, where T is the average interval between the impacts. Now, in a case like one where the average force acting on the system vanishes, as it would if the impacts were as many in one direction as the opposite, the velocity acquired would be proportional to p, and therefore the probability of the body acquiring a velocity v would be $\frac{\epsilon^{-\frac{v^2}{2n}}}{\sqrt{2n\pi}}$, *i. e.* would contain a factor of the form ϵ^{-kw}, where w is the kinetic energy, and w would not occur in any other factor. When this is so, k must be proportional to $1/w_0$, where w_0 is the mean value of w; so that the probability of the occurrence of the energy w is $\epsilon^{-\frac{w}{w_0}\cdot\alpha}$, *i. e.* the law of distribution is analogous to Maxwell's.

Since the probability for the value p is proportional to $\epsilon^{-\frac{p^2}{2n}}$, the mean value of p is proportional to $\sqrt{n}$, *i. e.* to $\sqrt{t/\Gamma}$, and thus would increase indefinitely with the time. We should, however, expect that in actual physical systems there would be agents at work which would tend to make the abnormal values of p die away to the normal one, and that ultimately the distribution of p among the different systems would get into a steady state and be independent of the time. We may represent the tendency to revert to the normal condition by supposing that the values of p when established die away with the time in such a way that, if p is the initial value the value of p after a time t is $\epsilon^{-kt}p$; thus $1/k$ may be taken as measure of the life of an abnormality. It is evident that for values of t considerable with respect to $1/k$, an increase in t will not produce any further increase in the abnormality, for a stage will be reached where the new abnormalities will be balanced by the decay of the old. We see from these considerations that if the probability for the value p is given by an expression of the form $\epsilon^{-\frac{p}{2n}}/\sqrt{2n\pi}$, n cannot be proportional to the time, but will approach a constant value as soon as t is considerable with respect to $1/k$. The distribution of abnormality will reach a steady state which we now proceed to investigate, in the simple case when the motion of the system is in one direction.

Let $f(p)$ represent the probability that a system has p impacts in excess of the normal. The systems which at any epoch have p impacts will have had at a time t before this epoch a different number, q, of impacts: let us see what is the condition that a system which began with q should end with p. Of the q impacts at the beginning, only $\epsilon^{-kt}q$ will remain at the end; hence, if it has p at the end, it must in the interval have received x impulses, where x is given by the equation

$$\left.\begin{aligned} \epsilon^{-kt}q + x &= p, \\ q &= \epsilon^{kt}(p-x). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The chance that a system should receive these impulses is

$$\frac{\epsilon^{-\frac{x^2}{2n}}}{\sqrt{2n\pi}};$$

hence the number of systems which are in the class p at

the end of the time t

$$= \sum_{-(1,2,3,\dots\infty)}^{+(1,2,3,\dots\infty)} f(q) \frac{\epsilon^{-\frac{x^2}{2n}}}{\sqrt{2n\pi}},$$

$$= \int_{-\infty}^{+\infty} f(q) \frac{\epsilon^{-\frac{x^2}{2n}}}{\sqrt{2n\pi}} dq \quad \text{approximately,}$$

$$= \int_{-\infty}^{+\infty} f(q) \frac{\epsilon^{-\frac{x^2}{2n}}}{\sqrt{2n\pi}} \epsilon^{kt}\, dx.$$

Since from (8) $dq = \epsilon^{kt} . dx$

$$= \int_{-\infty}^{+\infty} \epsilon^{kt} . f(\epsilon^{kt}(p-x)) \frac{\epsilon^{-\frac{x^2}{2n}}}{\sqrt{2n\pi}} . dx.$$

This number is, however, equal to $f(p)$; hence we have the equation

$$f(p) = \int_{-\infty}^{+\infty} \epsilon^{kt} . f(\epsilon^{kt}(p-x)) \frac{\epsilon^{-\frac{x^2}{2n}}}{\sqrt{2n\pi}} dx.$$

Let us see if this admits of a solution of the form

$$f(p) = \epsilon^{-hp^2}.$$

Substituting this value of f and integrating, we get

$$\epsilon^{-hp^2} = \epsilon^{-\frac{hp^2 . \epsilon^{2kt}}{2n\left(h\epsilon^{2kt} + \frac{1}{2n}\right)}} \frac{\epsilon^{kt}}{\sqrt{h\epsilon^{2kt} + \frac{1}{2n}}} \frac{1}{\sqrt{2n}},$$

an equation which will hold for all values of t if

$$\epsilon^{2kt} = 2n\left(h\epsilon^{2kt} + \frac{1}{2n}\right),$$

i. e.

$$n = \frac{\epsilon^{2kt} - 1}{2h\epsilon^{2kt}}.$$

If t is infinite,

$$n = \frac{1}{2h};$$

while when kt is small,

$$n = \frac{kt}{h}.$$

But when kt is very small,

$$n = \frac{t}{T},$$

where T is the interval between two impacts—the time-interval of the force. Hence

$$h = k\mathrm{T} = \frac{\text{(time-interval of the force)}}{\text{life of an abnormality.}}$$

Hence we see that, when certain conditions are fulfilled, a Maxwellian distribution of energy among the molecules may, when the forces are intermittent, be produced without the aid of collisions between the molecules. The number of molecules which have energy of a certain value will be given by the same expression as if the distribution had, as on the Kinetic Theory of Gases, been brought about by collisions. The molecules with the high energy content will, however, not have acquired this energy by collision with other molecules, but by drawing on the energy in the fields of force of the molecules ; molecules with more than the average energy have abstracted energy from these fields, while those with less than the average energy have given up energy to them. Thus the Conservation of Energy holds on the average for a large number of molecules, though it does not hold for individual molecules. When the energy is acquired in this way, the rate at which it is acquired will not be determined by the number of collisions or by the intensity of the radiation, and we escape the very formidable difficulty already alluded to, that the rate of communication of energy by radiation to the molecules of N_2O_5 is not nearly large enough to account for the energy which, according to the experiments of Hirst and Rideal, is absorbed in the decomposition of N_2O_5.

On the preceding theory the law of distribution of the velocities is similar to that of Maxwell ; so that if M is the number of molecules of the reacting substance, the expression for the number which possess energy adequate for the reaction is of the form

$$\mathrm{M}p\epsilon^{-\frac{aw}{\mathrm{R}\theta}}.$$

This is on the assumption that the average energy is proportional to $\mathrm{R}\theta$. p is a quantity which may depend on $w_0/\mathrm{R}\theta$ and also, as in the case of collisions, on the number of atoms in the molecule and their capacity for the storage of energy. The rate of decomposition depends, however, on the number which attain the critical energy in unit time, rather than upon the number which have this energy when things are steady. We can find the number which reach the active state in the following way. We

have supposed that the abnormal distribution dies away according to the law ϵ^{-kt}, so that $1/k$ may be taken as the life of the molecules in a special state; hence the number of activated molecules which disappear in the time δt is

$$\mathrm{M}p\epsilon^{-\frac{aw}{\mathrm{R}\theta}}.\frac{\delta t}{1/k}.$$

But when things are in a steady state, the number which leave any special distribution must be the same as the number which reach it. Thus the number which reach activated state in the time δt must be

$$\mathrm{M}p\epsilon^{-\frac{aw}{\mathrm{R}\theta}}.\frac{\delta t}{1/k};$$

so that, by (4), the rate of the reaction when the pressure is very low is equal to

$$kp\epsilon^{-\frac{aw}{\mathrm{R}\theta}}.$$

Since the distribution of velocities follows Maxwell's law, the investigation on p. 247 will apply, so that when the number of the atoms in the molecule is n, the value of p is

$$\frac{\epsilon^{\frac{3(n-1)}{2}}\left(\frac{w_0}{\mathrm{R}\theta}-\frac{3(n-1)}{2}\right)^{\frac{3n-2}{2}}}{\Gamma\left(\frac{3n}{2}\right)}.$$

Hence the rate of the reaction for N_2O_5 when $n=30$ and $w_0/\mathrm{R}\theta=50$ is

$$2k\times 10^6\epsilon^{-\frac{w_0}{\mathrm{R}\theta}}.$$

By Hirst and Rideal experiments this rate is equal to

$$2{\cdot}53\times 10^{14}\epsilon^{-\frac{w_0}{\mathrm{R}\theta}}.$$

Hence $k=1{\cdot}26\times 10^8$; so $1/k$, the time of decay of the abnormality, is equal to 8×10^{-8} second.

When $w_0/\mathrm{R}\theta$ is large, p at first increases rapidly with n; it reaches a maximum when

$$\frac{\Gamma\left(\frac{3n+3}{2}\right)}{\Gamma\left(\frac{3n}{2}\right)}=\left(\frac{\epsilon w_0}{\mathrm{R}\theta}\right)^{\frac{3}{2}}\quad\text{approximately.}$$

The rate of the reaction both at high pressures and at low ones will *ceteris paribus* increase with the number of atoms in the molecule until this number is reached; it will then diminish as the number of atoms increases.

XXV. *The Mobility of Ions in Solution, with particular reference to the Separation of Isotopes* *. *By* Eric R. Jette, *Ph.D., Assistant Professor in Washington Square College, New York University* †.

A NUMBER of articles ‡ have appeared during the last few years discussing the possibility of the separation of isotopes by methods depending upon an assumed influence of the different masses of isotopic ions on their mobilities in solution. The writer has been led to inquire whether it is at all reasonable to postulate such a "mass effect" on the electrical mobility of dissolved ions and has examined the available experimental and theoretical material from this viewpoint.

Introduction.

Let us first consider what is understood under the term "ion" according to our present knowledge of atoms and molecules. An ion may be described as an electrically charged particle which has been formed by the electrolytic dissociation of a chemical molecule §. An unsolvated ion has a definite mass and volume. Regarding its behaviour with respect to the solvent in which it is immersed, we can consider two of its effects on the solvent molecules although it may not be possible to distinguish sharply between them. The first of these is due to the electrical charge of the ion which, for reasons of mathematical simplicity, must be considered as distributed on the surface of the ion. Since we do not know the shape of the ion, we cannot say anything quantitative about the distribution of the charge. We know that the molecules of ionizing media have electrical moments ‖, and thus tend to orient themselves in the vicinity of a

* Contribution from the Havemeyer Chemical Laboratories of Columbia University, Number 524.

† Communicated by Prof. Sir Jas. Walker, D.Sc., Ph.D., F.R.S.

‡ Lindemann, Proc. Roy. Soc. Lond. A, xcix. p. 102 (1921). Kendall and Crittenden, Proc. Nat. Acad. Sci. ix. p. 75 (1923). Kendall and White, *ibid.* x. p. 458 (1924). Pilley, Phil. Mag. xlix. p. 892 (1925). Aston, 'Isotopes' (London 1924), p. 172.

§ This is not intended as a rigorous definition, but chiefly to give a rough distinction from a colloidal particle carrying a charge secured by the adsorption of an ion from solution.

‖ Debye, *Phys. Zeit.* xiii. p. 97 (1912). *Cf.* also the references in footnote ‡, p. 265.

charged particle such as an ion. The distribution of the charge will determine the form of the ion aggregate, and the surface density of the charge the intensity of attraction between the ion and the solvent molecules. This property therefore consists of the purely electrostatic effects of a charged particle on the molecules of the medium. It depends on the charge, the surface area and the shape of the ion.

Besides the purely electrostatic attractions, there are in many, and perhaps all, cases more or less specific attractions between the ion and the solvent molecules which is expressed, at least in part, by the Werner coordination number and which would, therefore, be classed as "chemical" attraction. It is unnecessary to speculate upon the nature of the forces causing this more specific effect. It is only necessary to point out that nothing can be predicted regarding the variation of this property among different ions in the same solvent nor for the same ion in different solvents, except possibly when the ions or solvents are very similar in other chemical properties.

The mobility of an ion may conceivably be dependent upon (*a*) the volume of the ion or the aggregate which actually moves through the solvent, which in turn depends upon the volume and shape of the non-solvated ion and upon the specific relations between ion and solvent, and (*b*) the mass of the ion or ion aggregate.

Isotopes have been shown to possess atomic volumes which are identical within the limits of experimental error *. The shapes of the ions are, therefore, presumably the same. All of the work on the separation of isotopes by chemical means and the more recent work on the spectra of isotopes indicates quite clearly that the primary chemical forces (valence forces, in particular) are the same to such a high degree that differences in the secondary or coordinative forces are not to be expected.

Thus from the standpoint of ionic mobility, isotopes would differ only in the masses of their individual ions. Whether or not it should be possible to separate the isotopes of a given element by means of differences in their ionic mobilities therefore depends upon the effect of mass on the mobility of an ion. Certain experimental evidence has been found and certain theoretical considerations have been

* Soddy, Nature, xciv. p. 615 (1915); Richards and Wadsworth, J. Am. Chem. Soc. xxxviii. p. 2221 (1916); Aston, 'Isotopes,' p. 166–7: a summary of the results on the spectra will be found on p. 151 *et seq.* See also P. Das, Chem. Abs. xviii. p. 2281 (1924).

formulated which might indicate that such an effect would be expected. Our task is to analyse this material. We shall consider first Lindemann's treatment of the problem, second, certain empirical relations derived from experimental results, and third, the results of the application of kinetic and of hydrodynamic theory.

Lindemann's Equation.

The only equation which has been derived for the express purpose of representing the separation of isotopes by the method of ionic migration is given by Lindemann (*loc. cit.*), who pictures the progress of an ion through a solvent medium in somewhat the following manner:—An ion moving under the influence of an electric force F is continually opposed in its forward motion by collisions with solvent molecules. If the velocity of an ion just after a collision with a solvent molecule is given by V_1, and the electrical force acts on the ion between two collisions during the time t required by the ion in travelling over its mean free path, and further if the univalent ion of mass M retains the fraction $\frac{M}{M+m}$ of its momentum after colliding with a solvent molecule of mass m, then the residual velocity V_1 after the collision is given by

$$V_1=\left(V_1+\frac{Ft}{M}\right)\frac{M}{M+m} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It is the second term inside the parenthesis which we shall examine more closely.

The product *force* × *time* = *impulse* and this is related to momentum according to $Fdt=MdV$ which, upon integration, and setting $V=0$ when $t=0$, yields $Ft=MV$. Lindemann has applied this equation in the form

$$V_e=\frac{Ft}{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in his kinetic considerations, so that (1) is really an expression of a case where the residual velocity after collision is equal to the sum of the residual velocity after the preceeding collision (V_1) and the velocity V_e due to the electrical field multiplied by the ratio $\frac{M}{M+m}$. It is unnecessary to repeat the remainder of the derivation which finally gives

$$\frac{1}{V}\frac{dV}{dM}=\frac{1}{2M}\frac{2M-m}{2M+m} \quad . \quad . \quad . \quad . \quad . \quad (2')$$

The problem then becomes to determine from experimental results and from independent theoretical considerations whether the velocity of a univalent ion in a solvent medium is really represented by $\frac{Ft}{M}$, by some function of this quantity, or by some other function of M.

Empirical Relations.

Walden * has found for a number of electrolytes in various solvents that the relation

$$\lambda_\infty \eta_\infty \sqrt{M} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

holds within experimental error; λ_∞ = molecular conductivity at infinite dilution, η_∞ viscosity of the pure solvent, M molecular weight of the solute. Since, according to Kohlrausch, $\lambda_\infty = u_a + u_c$ where u_a and u_c are the mobilities of the anion and cation, Walden finds further that

$$u_a \sqrt{M_a} = \text{const.} \quad \text{and} \quad u_c \sqrt{M_c} = \text{const.} \quad . \quad . \quad (4)$$

While these equations are undoubtedly of value as empirical rules, have they any theoretical significance?

Walden gives a derivation of (3) in the following manner:—Reicke † has shown that the diffusion coefficient D is given by

$$D\sqrt{M} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Herzog ‡ has shown that if we consider the diffusion of a substance in several different solvents, the following expression is obtained

$$D\eta = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

By combining these two Walden finds $\eta \sim \sqrt{M}$, and is also able to state that

$$D\eta \sqrt{M} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Since $\lambda_\infty \eta_\infty = \text{const}$ for a given electrolyte in a series of

* *Zeit. Elektroch* xxvi. p. 65 (1920). See also 'Electrochemie,' Leipzig 1922, p. 170 *et seq.* A critical review of Walden's work on the mobility of electrolytic ions has appeared since the present article was prepared (H. Ulich, *Fortschr. d. Chem.* xviii. no. 10 (1926).

† *Zeit. f. phys. Chem.* vi. p. 564 (1890); see also Jellinek, *Lehrb. Physikalischen Chemie*, ii. p. 895.

‡ *Zeit. Elektroch*, xvi. p. 1003 (1910).

solvents and, according to Walden, the resistance of dissolved electrolytes is determined by the viscosity of the solvent and the diffusion constant of the solute, equation (3) is obtained *.

The theoretical significance of (3) may be questioned on several grounds. First, it is to be noted that by applying purely kinetic considerations Reicke found that

$$D = k\frac{L}{\sqrt{M}},$$

where L is the mean free path of the dissolved particle and k is a constant, and not equation (5) as given by Walden. In certain cases it may be permissible to include L in the constant †, but this procedure certainly cannot be generally applicable.

Second, Herzog used purely hydrodynamic considerations ‡ in deriving (6). The relation $\lambda_\infty \eta_\infty = \text{const.}$ has also been derived by means of hydrodynamic but not by kinetic considerations. Since the fundamental assumptions of the hydrodynamic and kinetic theories, as far as liquids are concerned, are almost diametrically opposed, equations such as (3) and (7), in which they are directly combined, can have no theoretical significance. Third, the difference between equations (3) and (7) lies essentially in the substitution of λ_∞ for D. Objection therefore can be raised to splitting λ_∞ into two parts corresponding to the mobilities of the two ions, because this logically implies that the same process must be applicable to D. Nernst § in deriving the relation

$$\frac{1}{D} = \left(\frac{1}{u_a} + \frac{1}{u_c}\right)\frac{1}{2RT}$$

shows very clearly that one cannot consider the diffusion of the two ions of an electrolyte separately. In other words, the diffusion of the electrically neutral pair of ions is involved. Nernst's derivation is independent of any postulates regarding the velocities of the ions.

Fourth, in all three series of compounds which Walden has used as evidence for his rule, an increase of molecular or ionic weight is associated with an increase of molecular or

* η_∞ in (3) and η in (7) both represent the viscosity of the pure solvent.

† The reference to Reicke's work indicates that this is exceedingly doubtful. (See Table 149, p. 895 in Jellinek, *loc. cit.*).

‡ *I. e.* some form of the Stokes-Kirchhoff relation, equation (9).

§ Nernst, 'Theoretical Chemistry,' 1916 Ed. p. 398 *et seq.*

ionic volume *. In two of the series, the fatty acid anions and the tetra-alkyl ammonium iodides, the ratio $\frac{\sqrt{M}}{\sqrt[3]{v}}$ is very nearly constant for each series †. In the third series, a number of moni-, di- and trialkyl substituted ammonium ions, there is a fairly regular increase in the value of this ratio with increase in ionic weight. Thus in the case of saturated and of highly symmetrical ions the products ‡ $\lambda_x \sqrt[3]{v}$ and $u_a \sqrt[3]{v_a}$ are quite as constant as the corresponding products with $\sqrt{M}$. Since $\sqrt[3]{v}$ does not necessarily represent the radius to be inserted in equation (9), the variations of $u_c \sqrt[3]{v_c}$ appearing in the third series are not surprising, especially in view of the fact that they are found to be fairly regular for each type of compound. The constancy of the products containing $\sqrt{M}$ for these ions and compounds must therefore be considered as fortuitous.

Kinetic and Hydrodynamic Theories.

It is difficult to approach the problem of ionic mobility from the theoretical side because it seems quite impossible to avoid an arbitrary assumption whether the velocity is to be represented by the equations of kinetic theory or of hydrodynamic theory. Mass appears in the former, but not in the latter; for liquids, viscosity appears only in hydrodynamic theory. On other grounds as well, the two theories appear to be irreconcilable for the conditions with which

* There is only one exception, and in this case both substances have the same ionic weight. The inverse order of mobility with volume is also disturbed in this case, but since the one compound is a trialkyl and the other a dialkyl substitution product of NH_4^+, such a discrepancy is not remarkable. The volumes used were taken from Lorenz, 'Raumerfüllung u. Ionenbeweglichkeit,' Leipzig, 1922, pp. 16–18, or determined by Kopp's rule, arbitrarily setting the value for nitrogen as 4·5. Similar calculations cannot be made for NH_4^+ and H^+ which Walden also includes. However, the product $u\sqrt{M}$ for NH_4^+ is low, and H^+ is so exceptional in its mobility and general properties that the agreement of its value of $u\sqrt{M}$ is of doubtful significance. *Cf.* Eucken, Jette, and LaMer, 'Fundamentals of Physical Chemistry' (McGraw-Hill, 1925), pp. 444-5.

† Hevesy, *Jahrb. Radioakt. u. Elektr.* xiii. p. 276, footnote 5 (1916), points out the empirical nature of equation (5) when applied to ionic mobilities in solutions. He also states that for many organic compounds $\sqrt{M} \sim R$, where R is the radius of the molecule.

‡ *Cf.* Walden, 'Elektrochemie,' p. 171.

we are concerned. The only method of approach thus seems to be to consider the difference between the gaseous and liquid states and to determine from the limits of validity of the equations which of the two sets of postulates is to be preferred.

Lenard considers * that the difference between the gaseous and liquid states, as far as kinetic theory is concerned, lies chiefly in that the space occupied by the molecules of the medium cannot be neglected in the case of liquids. He therefore inserts a "free space factor" (ψ) into his gas kinetic equation, obtaining

$$\omega = V = \frac{F}{D\pi W s^2} \cdot \frac{\mu + (1-\mu)\frac{4}{\pi}}{\sqrt{\mu}} \cdot \frac{3}{3+\mu} \psi \quad . \quad . \quad (8)$$

where W = mean (linear) velocity of the gas molecules, $s = R + r$, D = N, m = gas density, $\mu = \frac{M}{M+m}$, M = mass of the ion.

H. F. Mayer † compares the migration velocities in water calculated by this equation with those calculated by the Stokes-Kirchhoff equation ‡

$$V = \frac{F}{6\pi\eta R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

He finds that equation (9) gives velocities lower than those found by equation (8) for particles of radii less than 10×10^{-8} cm., and both are of the same order of magnitude. Between 5×10^{-8} and 15×10^{-8} both equations give about the same values, while the extrapolation of both into this range shows that their curves intersect at a very small angle. According to certain theoretical considerations, the upper limit for equation (8) in liquids is $R \leqq 2r$, where R is the radius of the particle and r that of the medium molecules, and the lower limit of (9) is $R \geqq 6r$. If water is the solvent equation (8) should hold up to radii of about 5×10^{-8}, and therefore Mayer concludes that this is the equation which should apply to the simpler electrolytic ions which are supposed to have radii smaller than this value.

* Lenard, *Ann. d. Physik*, lxi. p. 665 (1920).

† *Jahrb. Radioakt. u. Elektr.* xviii. p. 201 (1921), particularly p. 233 *et seq.* See also Lenard, *loc. cit.*

‡ The most recent discussion of this equation is given by Weyssenhoff, *Ann. d. Physik*, (4) lxii. p. 1 (1920). His results are summarized by Lorenz, *loc. cit.* p. 197. A second paper by this author has appeared (*Bull. Acad. Polonaise Sci. et Lettres*, no. 7 *a*, p. 219 (1925) with the title, "Brownian Motion and Stokes' Law." Unfortunately, only abstracts of this article are available at the time of reading the proof (see Chem. Abs. p. 309, Oct. 10, 1926), but it was inferred that there is no essential conflict with the views expressed in the present paper.

Any conclusion in the matter seems to be largely a matter of opinion, for a number of writers do not adopt this view. As far as the data are concerned, the phenomena are so complex that no one claims very much more than that the radii of the ions calculated from mobility data are of the right order of magnitude.

The usual objection to applying the Stokes-Kirchhoff equation to ions moving in a solvent is that the ionic radius is not large in comparison with the radii of the medium molecules. Lorenz *, however, considers that the solvent medium is not discontinuous in any ordinary sense but that due to the attraction between the solvent molecules, a solvent presents a continuous, although not necessarily uniform force field to an ion moving through it and this field opposes the motion of the ion. Such an opposing force is not taken into account by ordinary gas-kinetic equations and certainly not compensated by a "free space factor." With regard to ions in solution, we are thus compelled either to neglect the collisions between ions and solvent molecules † or to neglect the force field between the solvent molecules since in the present state of the theories it seems impossible to consider both.

Born and Debye and Hückel ‡ disregard the effect of collisions, considering only forces depending upon the ionic radii and not those depending upon ionic mass §. Lorenz ‖ believes he has shown that the range of the applicability of the Stokes equation extends down to radii of about $3{\cdot}0 \times 10^{-8}$. Hevesy ¶ has shown that charged particles in a solvent tend to establish a certain minimum, approximately constant potential against the solvent, and in order to do this in the case of aqueous solutions, a very small univalent ion attaches a "shell" of water until its radius is about $2{\cdot}8 \times 10^{-8}$ cm. **.

* Lorenz, *loc. cit.* p. 203.

† Or else assume that the effect of these collisions over a long time can be neglected.

‡ Born, *Zeit. Physik*, i. p. 221 (1920); also Schmick, *ibid.* xxiv. p. 56 (1924). Debye and Hückel, *Physik. Zeit.* xxiv. p. 305 (1923). See also Eucken, Jette, and LaMer, *loc. cit.* p. 301 *et seq.* and p. 443 *et seq.*

§ In the derivation of an equation for molecular conductance P. Hertz introduces the mass of the ion, but in the final equation this factor cancels out (*Ann. d. Physik*, (4) xxxvii. p. 1 (1912)).

‖ Lorenz, *loc. cit.* p. 5.

¶ Hevesy, *Koll. Zeit.* xxi. p. 129 (1917). Born, *loc. cit.* p. 222 footnote, considers Hevesy's earlier work to be theoretically improbable and inconsistent with Lorenz; see, however, Lorenz, *loc. cit.*, p. 237 *et seq.*

** The combination of this result with that of Lorenz indicates that when the nonsolvated ion is too small for its motion to be considered from the hydrodynamic viewpoint, the effect of the high surface density of its charge insures that the dimensions of the aggregate which actually moves in the electrical field are sufficiently great for a hydrodynamic treatment to be valid.

He also considers that it is practically only the radius which determines the velocity of diffusion of an ion *.

If we take a series of ions for which the specific effects on a given solvent are approximately the same, the effect of varying size and thus of electrostatic effects can be calculated in a fairly satisfactory manner, as Born † has done for the alkali metal ions. For non-aqueous solvents, the relative order of mobilities or of molecular conductivities under comparable conditions, for these ions is, in general, the same as in water, *i. e.*

$$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Rb} < \mathrm{Cs}.$$

In the case of the simpler anions, inversions of the order in different solvents are more frequent. This is all that the somewhat meagre experimental data allow us to state. It is quite certain, however, that it is not logical to compare the relative order of mobilities of arbitrarily chosen ions in one solvent with that in another solvent and expect to find agreement ‡.

A survey of the field of ionic migration indicates that while equations based upon hydrodynamic theory, and thus involving the Stokes-Kirchhoff relation, are not in entire accord with experimental facts, the deviations between theory and experiment are not to be accounted for by means of introducing the mass of the moving ions, but rather by taking into account (*a*) the specific interactions between the ion and solvent molecules §, (*b*) the effect of changes in dielectric constant of the medium arising from the presence of the charged particles and change of temperature, and (*c*) the effect of variations in the dielectric constant and heat motion upon the purely electrostatic attractions between the electrically charged ions and the molecules of the solvent. None of these depend upon the mass of the ion. At the present time we have no means of taking into account, in any adequate manner, the variations and the effects of all three of these factors. Presumably, kinetic theory could

* Diffusion may be considered as a motion determined by a concentration gradient, while electrical mobility is determined by a potential gradient. With respect to the rates of diffusion of isotopic ions, Murmann (*Oestr. Chem. Zeit.* xxvi. p. 14 (1924) concludes, from his experimental results, that they must be the same and independent of differences in mass.

† *Loc. cit.* Born is able to calculate the correct relative order of ionic radii, which is reversed by the straightforward application of equation (9).

‡ *E. g.*, Kraus, "Properties of Electrically Conducting Systems." Chem. Cat. Co. pp. 202-204.

§ See Kraus, *loc. cit.* p. 204. line 4 *et seq.*, where this point is emphasized.

explain to some extent the first and third effects by assuming a certain fraction of the collisions between ions and solvent molecules to be "inelastic," as is done in the case of gases by the Cunningham correction to the Stokes equation (*cf.* Proc. Roy. Soc. (Lond.) A, lxxxiii. p. 357 (1910)). For the present case of ionic mobility in solution, this sort of treatment is not very promising, since it would involve entirely arbitrary assumptions regarding the structure of the ion aggregate, its "dynamic" or "static" character, and its stability. Direct experimental test of such assumptions is not possible. By assuming certain degrees of hydration the mass factor in equation (8) can be changed at will and, without extending such assumptions much beyond the range of reasonable probability, it is possible to secure very good agreement with the experimental results. It is to be emphasized that such a treatment does not solve the difficulty completely because the resulting increase in mass is always accompanied by an increase in volume, which means that the more hydration we assume the more closely we approach the conditions demanded by hydrodynamics. The agreement between the hydrodynamic equations and the experimental results in general improves as the size of the ion increases and, for the larger organic ions, the agreement seems to be satisfactory *. The variations observed with the smaller ions can be accounted for only when we know more about the relationship between an ion and the solvent medium.

Lindemann's equation (2′), when applied to the lead isotopes of mass 206 and 208, indicates a difference in mobility of 0·44 per cent. According to equation (8) the mobilities of these ions should differ about 0·1 per cent. Pilley †, who uses equation (2), but takes into consideration the relative velocities of ion and solvent molecules in the calculation of t, arrives at an equation which gives a difference of 0·032 per cent. These results are for the most favourable case, where the ions are not solvated. It is apparent that as the kinetic treatment of the problem is refined to take into account those factors which would be involved in closer approximations to the actual state of affairs when an ion moves through a solution, the expected difference in the mobilities of ions, due to their different masses, becomes smaller and smaller.

Hevesy and Paneth ‡, from a study of galvanic cells of

* *Cf.* Lorenz, *loc. cit.* p. 75 *et seq.*

† *Loc. cit.*

‡ *Wien. Ber.* cxxiv. p. 381 (1915). See also Hevesy, *Jahrb. Radioakt. u. Elektron.* xiii. p. 289, footnote 1 (1916). The Lenard equation u by Hevesy is an older one, since modified to give (8).

the lead isotopes, conclude that the mobilities would differ by less than 0·01 per cent. According to the Stokes-Kirchhoff equation they should not differ at all. No measureable separation of isotopes based upon difference of ionic mobility in solution has been accomplished up to the present, although a number of attempts have been made. (*Cf.* Pilley, *loc. cit.*, Kendall and White, *loc. cit.*).

Kendall and White have shown that with I^- and Cl^- ions, which have a mobility difference of 1·4 per cent., only a partial separation resulted even after a migration of 900 cm. More recent work in the Havemeyer Laboratory of Columbia University on the separation of Zr from Hf, indicates that here also only a very small degree of separation is experimentally possible *. In each of these two pairs of ions there are certainly greater differences in chemical properties and in ionic volumes than exist between isotopic ions.

It is evident that although a complete and adequate kinetic treatment of the problem might indicate that a "mass effect" on the mobility of ions should or should not exist, this problem is one which can only be decided finally on the basis of very careful experimentation in which the experimental error in the determination of the ionic mobilities or conductances is 0·001 per cent. or less †. This is beyond the accuracy of our present experimental methods.

The ionic migration method certainly offers no such degree of accuracy, whether performed in aqueous solutions or in gels, due chiefly to the difficulty in finding methods of detecting small degrees of separation, even in the case of radioactive isotopes. Under very favourable circumstances it is sometimes possible to measure the conductance of a solution and duplicate results on the same solution to this degree of accuracy. The duplication to 0·001 per cent. with two solutions made up independently of materials from different sources, even when saturated solutions of salts of limited solubility (*e.g.* $PbSO_4$ or $PbCl_2$) are used, is doubtful. Up to the present time, lead is the only element whose individual isotopes have been secured in any significant quantity suitable for such an experimental test, and even here a difference in the measured conductance would not be an unequivocal demonstration that isotopic ions have different mobilities.

* Kendall and West, J Am. Chem. Soc., xlviii. p. 2619 (1926).

† That this is not an unreasonably high degree of accuracy to require will be clear when we remember that the above calculations were all based upon the most favourable case where the ions are not hydrated; hydration decreases the percentage difference in mass.

Summary.

Summarizing the situation with regard to the effect of the mass of the ion on its mobility, it has been shown :—

(1) Even if kinetic theory is applicable to an ion moving in a solvent, it is certain that the velocity due to an electrical field is not represented by such a simple relation as $\frac{Ft}{M}$ (for univalent ions).

(2) Walden's equations (3) and (7) cannot be derived except by combining two entirely different and, as far as liquids are concerned, apparently irreconcilable sets of fundamental assumptions.

(3) The agreement between experimental results and equations (3) and (7) is partly fortuitous and partly due to the fact that in some series of closely related organic compounds, such as were used in testing these equations, we have the condition that $\sqrt{M} \sim \sqrt[3]{v}$.

(4) While the experimental evidence from ionic mobility, molecular conductance, and diffusion does not give unequivocal support either to the hydrodynamic or to the kinetic theory, the present tendency seems to be to extend the range of applicability of the Stokes-Kirchhoff equation to smaller particles rather than that of the kinetic equations to larger particles. Furthermore, in ionizing solvents the relations between ion and solvent involve specific interactions and electrostatic effects, and there are cohesive forces acting between the solvent molecules themselves; all of these are independent of ionic mass and therefore are not completely taken into account by kinetic considerations.

(5) While no final decision upon the existence or non-existence of a "mass effect" can be made at present, since the requisite adaptation of the two main theories to the conditions existing about an ion in a solvent medium has yet to be made, it is quite certain that any difference in the mobilities of isotopic ions is exceedingly improbable. If a difference does exist, it must be of an extremely low order of magnitude.

(6) It is certain that an experimental detection of a difference in the mobility of isotopic ions in solution is impossible by any method available at the present time.

In conclusion, the author wishes to thank Professor James Kendall for suggesting to him the necessity of an analysis of the problem of the mobility of isotopic ions, such as has been attempted in this article.

New York, N.Y., U.S.A.

XXVI. *On Tables of Elliptic Functions.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the October number 1926, p. 827, there is a statement by Professor W. B. Morton that he has been unable to find a tabulation of the Jacobian elliptic function of the second kind, Z nor $2nf\mathrm{K}$, the function $\mathrm{E}\phi$ of Legendre required in his article for the Parallel Plate Condenser in the expression of its conjugate functions.

I desire then to call attention to the stereotyped Table of the Elliptic Function calculated by Colonel R. L. Hippisley, and published recently in the volume of the Smithsonian Mathematical Formulæ, under the direction of Professor Edwin P. Adams.

Appendix XI, "Elliptic Functions," occupies the final pages of the volume, 245–309, result of Col. Hippisley's calculations. I have detached these pages, and bound them up in a separate little volume, to show how a number of them could be issued at once as specimens for immediate use. The calculation (to 10 figures) was a very formidable piece of work, and should be made familiar to all making applicaton of Elliptic Function work: this pamphlet volume is on my table up here, and could be forwarded for inspection. Meanwhile application could be made through Professor Adams, for permission for the temporary issue of these specimens to invite criticism and use.

The 8 functions in the columns are lettered A, B, C, D, E, $\mathrm{F}\phi$, G, $\mathrm{F}\psi$, in two facing pages, each of 45 lines to the 90 degrees in the modular angle θ to a quadrant of 90°. The Jacobian-Legendrian equivalents are

$$\mathrm{F}(r)=\mathrm{F}\phi, \qquad \phi=mf\mathrm{K}, \quad f=\frac{r}{90},$$

$$\mathrm{E}(r)=\mathrm{E}\phi, \qquad \mathrm{G}(r)=\mathrm{E}(90-r)=$$

$$\mathrm{D}(r)=\frac{\Theta f\mathrm{K}}{\Theta_0}, \qquad \mathrm{A}(r)=\frac{\mathrm{H}f\mathrm{K}}{\mathrm{H}\overline{\mathrm{K}}}, \qquad \mathrm{B}(r)=\mathrm{A}(90-r),$$

$$(\mathrm{C}r)=\mathrm{D}(90-r).$$

I think this arrangement will bear the test of immediate application. The calculation was a most formidable piece of work, and I feel some remorse at inflicting it on Col. Hippisley; but he took it up enthusiastically, and seems to bear me no grudge for the infliction of this terrific arithmetic.

Yours sincerely,

G. GREENHILL.

1 Staple Inn,
5th November, 1926.

XXVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. ii. p. 1287.]

May 19th, 1926.—Dr. F. A. Bather, M.A., F.R.S., President, in the Chair.

THE following communication was read :—

'The Carboniferous Limestone (Avonian) Succession of a Portion of the North Crop of the South Wales Coalfield.' By Thomas Neville George, M.Sc.

A description is given of the lithological and faunal succession of the Avonian along some 30 miles of the North Crop between Kidwelly and Penwyllt (Tawe Valley). The general succession is as follows :—

		Thickness in feet.
	Millstone Grit.	
	Unconformity.	
$D_2 D_3$	Upper Limestone Shales. Shales, with impure limestones weathering to rottenstone	0–20
	Main Limestone.	
D_2	Dark limestones of various types: east of the Kidwelly district they are associated with grits, thin quartzites, and abundant cherts	0–250
D_1	Pale-grey oolite. A coarse oolite, with a sandstone (the Honeycombed Sandstone) at the base	40–70
S_2	Limestones and oolites, with much pisolite	300–350
	Unconformity.	
K	Lower Limestone Shales. Shales, with thin limestones	15–100
	Unconformity in places.	
	Old Red Sandstone.	

The Main Limestone presents several interesting features. It is much attenuated, when compared with other areas, being about 500 to 600 feet thick. This is due to the following reasons :—

(1) An intra-Avonian unconformity, marked by the absence of the zones of Z (possibly K_2) to S_1, is present. It is probable that deposition recommenced early in S_2 times.

(2) The zones which are present are probably condensed, owing to intermittent deposition.

(3) In parts, overstep by the Millstone Grit cuts out some of the upper beds.

The Middle *Dibunophyllum* Zone is represented by two facies, which appear to have been deposited in more or less separate areas. That seen near the Kidwelly district consists of standard limestones yielding a normal fauna, and is comparable with beds of the same horizon in Gower, Pembrokeshire, Bristol, etc. The other consists of impure sandy and cherty limestones, with some calcite-mudstones, and a fauna chiefly composed of molluscs and Productids. As this facies is traced eastwards towards Llandebie it becomes more normal. The two areas of deposition were presumably

separated by a barrier resulting from an earth-movement in D times. This is indicated by overstep of the Millstone Grit in the district separating the two facies, where the greater portion of the *Dibunophyllum* Zone is absent.

It is evident that, throughout Avonian times, the area was subject to periodic earth-movements, evidence of some of which has been found in Gower and Pembrokeshire by Mr. E. E. L. Dixon. The effects of these movements are clearly seen in the area described, owing to its proximity to the Avonian shore-line.

XXVIII. *Intelligence and Miscellaneous Articles.*

SURFACE-TENSION BY THE METHOD OF RIPPLES.

To the Editors of the Philosophical Magazine.

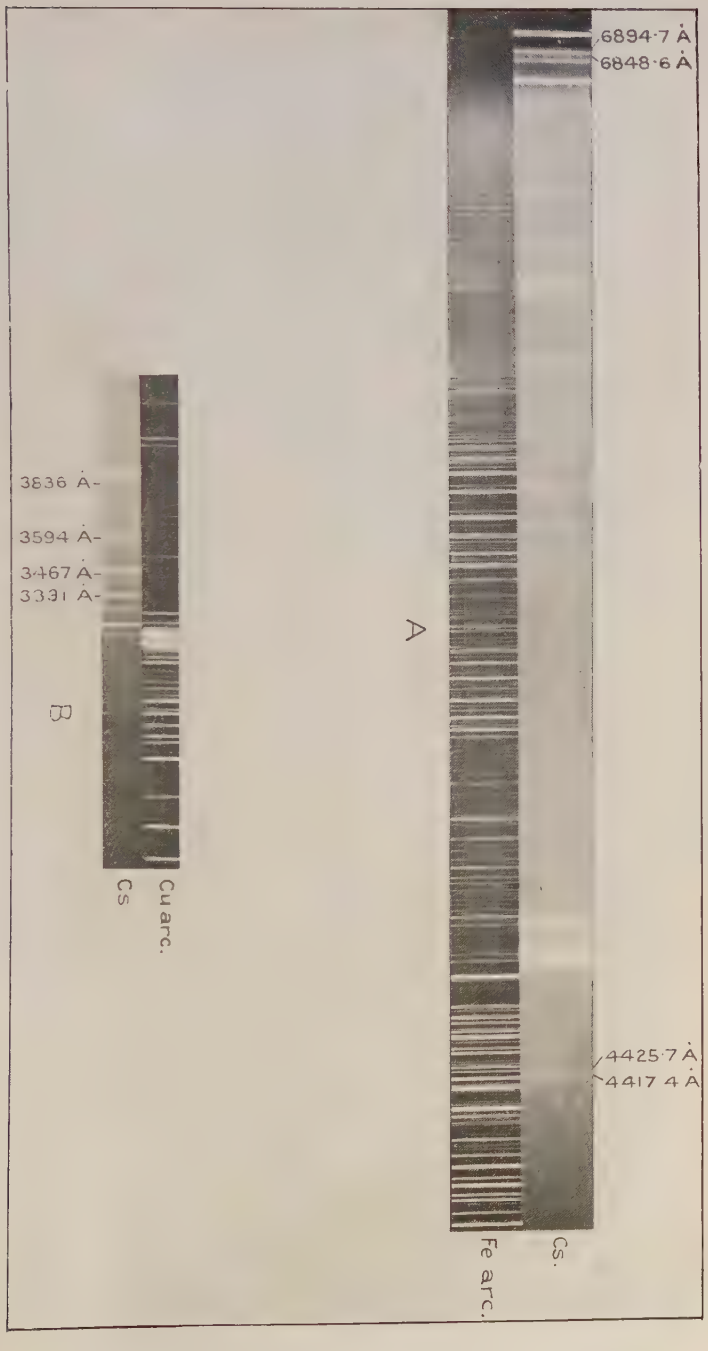
GENTLEMEN,—

MAY I point out that in the determination of the surface-tension of a liquid by the method of ripples by Messrs. Ghosh, Banerji, and Datta (Philosophical Magazine, June 1926), they claim to be the first to use a "device in which the stroboscopic effect was perfect inasmuch as a second fork was not necessary." This device has been in use for the last three years in the elementary classes of physics in the University of Toronto. We use an electrically maintained fork in series with a Rayleigh synchronous motor, both having been supplied by Pye & Co. of Cambridge. We have used forks of 100 d.v. and 200 d.v. per second, the ripples being excited by a mica sheet waxed to the lower prong of the fork, a sheet of the same size being affixed to the upper prong to keep its frequency the same as the lower prong. The ripples are observed through the sectors of the disk on the Rayleigh motor. Both water and mercury have been experimented with, and the students measure the wave-length by a small strip of millimetre scale held just over the liquid surface. Suitable lamps are placed to get the best reflexion. Reasonably accurate results have been obtained by the students, but of course there is no time in the ordinary laboratory period to aim at refinements. Results nearly as good have been obtained even by a single student by replacing the Rayleigh motor (which sometimes requires a larger current than that required to actuate the fork) by a variable speed motor carrying a disk pierced with a peep-hole near its circumference. The motor is speeded up until the wave pattern remains stationary, care being taken to run at the right speed and not at half-speed or a simple multiple of the speed, or other patterns will be observed.

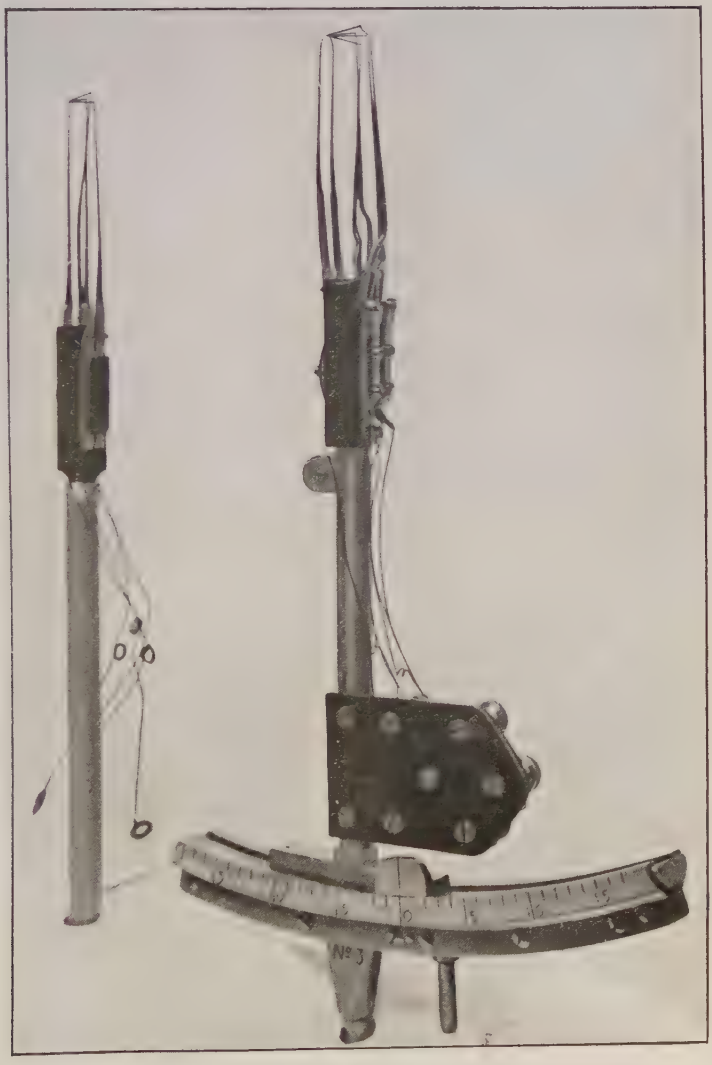
University of Toronto, Canada,
October 14, 1926.

Yours truly,
JOHN SATTERLY.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]


6894·7 Å
6848·6 Å
A
4425·7 Å
4417·4 Å
Fe arc.
Cs.
3836 Å.
3594 Å.
3·467 Å.
3331 Å.
B
Cu arc.
Cs

Figs. 17 *a* and *b*.



Hot-wire Speed and Direction Meters.

The figure on the left-hand side is an illustration of the three-wire instrument, whilst that on the right-hand side represents a four-wire instrument.

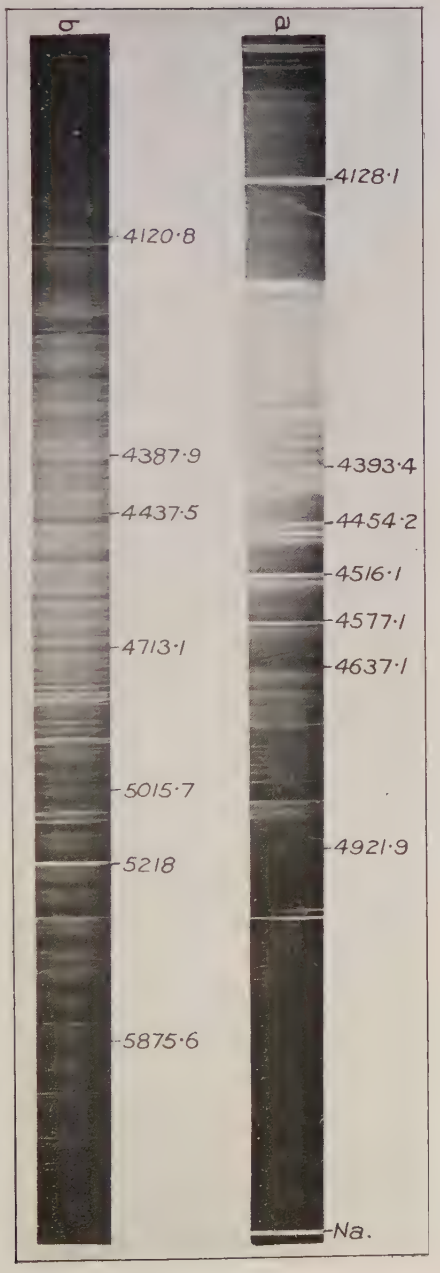
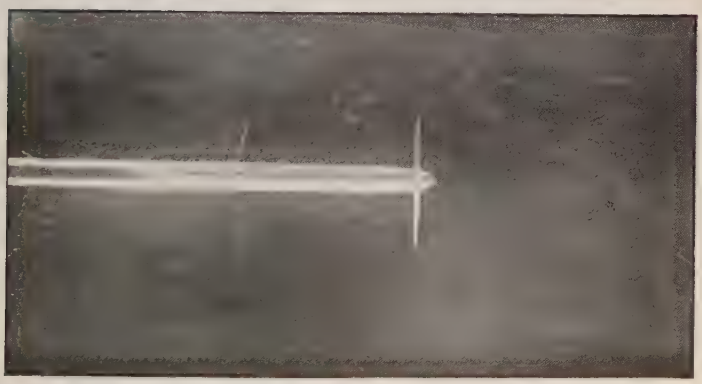

Cr
Fe
4128·1
4120·8
4387·9
4393·4
4437·5
4454·2
4516·1
4577·1
4713·1
4637·1
5015·7
4921·9
5218
5875·6
Na.

Fig. 2.

Photograph of model screw 1 inch diameter.

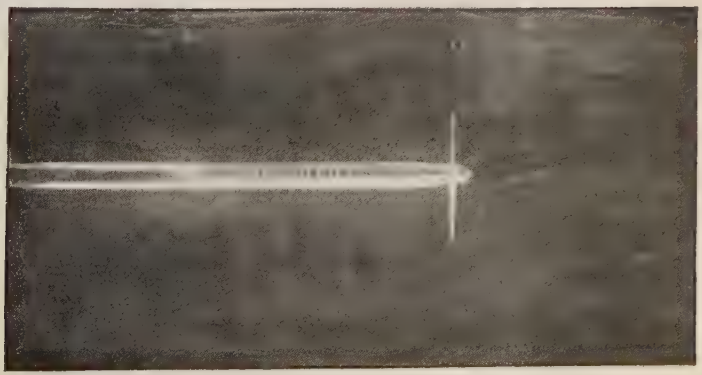
Fig. 3.



Direction of flow ←——

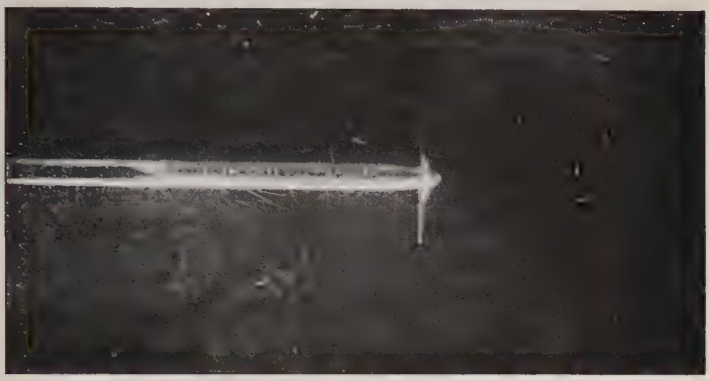
Rotational speed increasing ↓

Fig. 4.



Direction of flow ←——

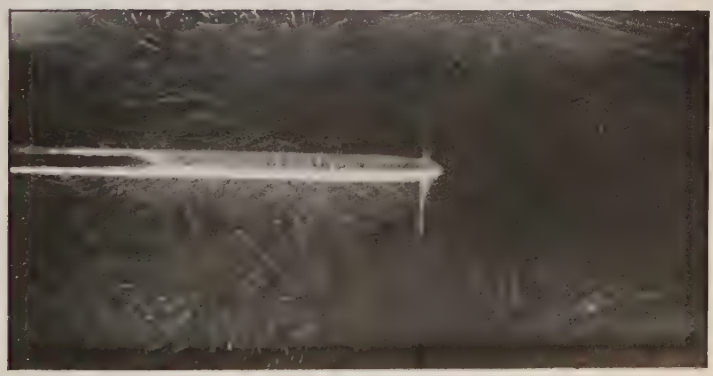
Fig. 5.



Rotational speed increasing ↓

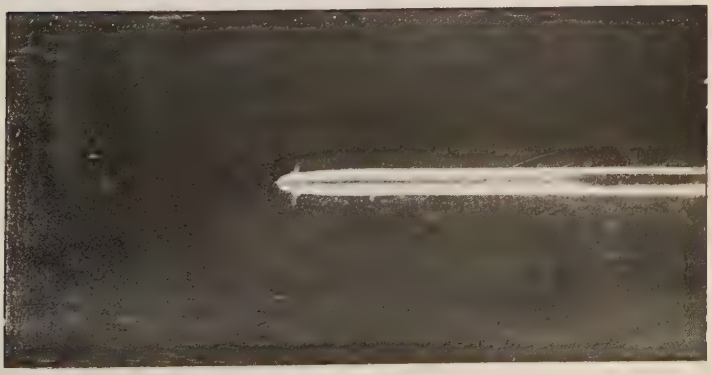
Direction of flow ←——

Fig. 6.



Direction of flow ←——

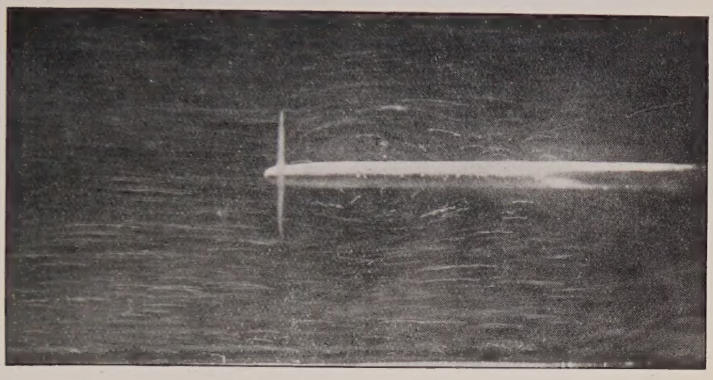
Fig. 7.



Screw at rest.

Direction of flow ——→

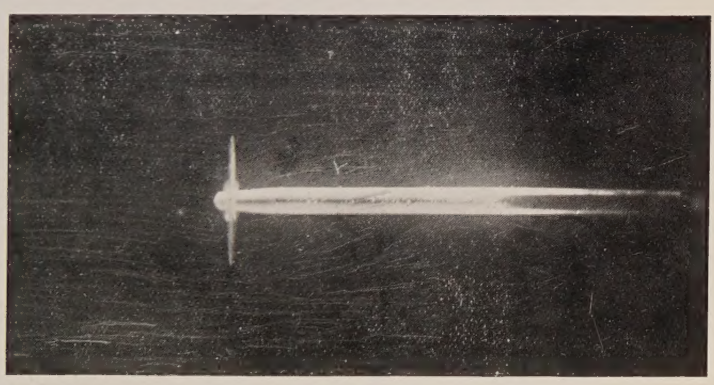
Fig. 8.



Rotational speed increasing ↓

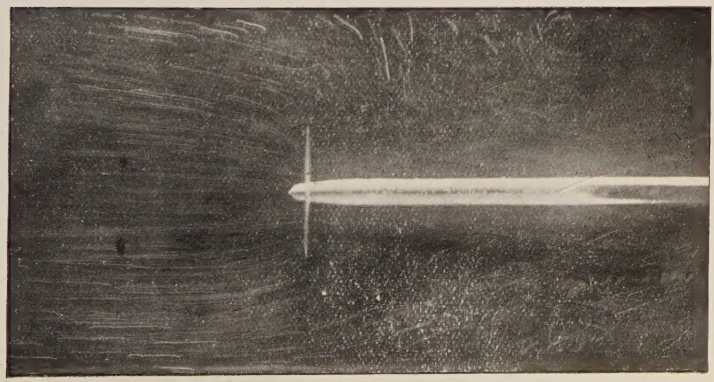
Direction of flow ⟶

Fig. 9.



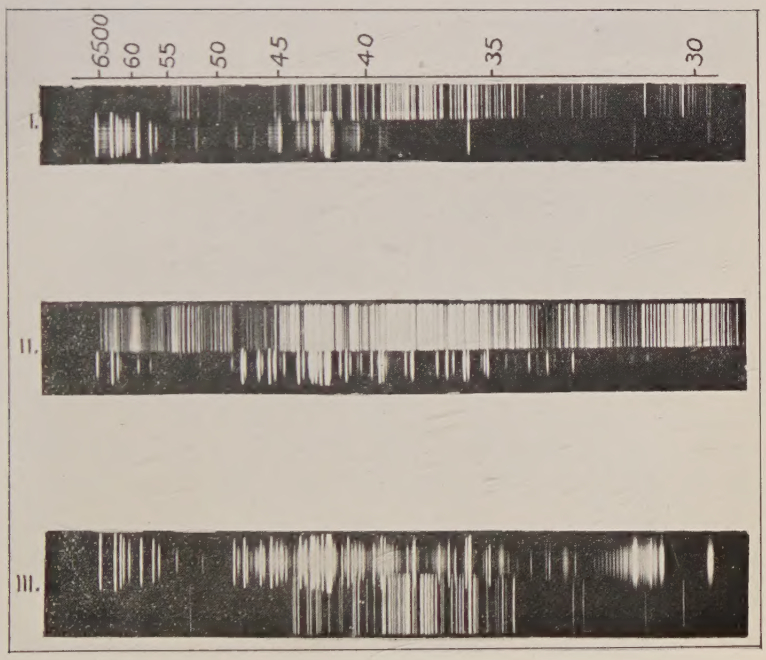
Direction of flow ⟶

Fig. 10.



Direction of flow ⟶

Flash Arc Spectrum of Rubidium.



I. Rubidium Arc with Iron Comparison.
II. Rubidium Flash Arc with Iron Comparison.
III. Rubidium Fluoride Flash Arc with Iron Comparison.